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SUBSTRATE AND POSITIONAL SELECTIVITY IN ELECTROPHILIC SUBSTITUTION REACTIONS OF PYRROLE, FURAN, THIOPHENE, AND SELENOPHENE DERIVATIVES*

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The relative reactivity (substrate selectivity) of five-membered heterocycles on electrophilic substitution (pyrrole >> furan > selenophene > thiophene) and their positional selectivity (furan > selenophene ≥ thiophene > pyrrole) are not consistent. The indicated differences in positional selectivity (α : β ratios) of the parent heterocycles show up essentially in orientation on electrophilic substitution reactions of their derivatives and the corresponding benzannelated systems. It was shown that the positional selectivity was reduced in a sequence corresponding to the change in relative stability of the onium states of the elements ($O^+ < Se^+ \leq S^+ < N^+$) and reflects the predominant role of the heteroatoms in stabilizing the σ-complexes formed on β-substitution, in which the positive charge is distributed between the heteroatom and one α-carbon atom (in α-isomers four atoms of the ring participate in delocalization of the charge). This interpretation was confirmed by quantum-chemical calculations carried out by the RHF/6-31G(d), MP2/6-31G(d)//RHF(6)-31G(d), and B3LYP/6-31G(d) ab initio methods.

Keywords: benzo[*b*]selenophene, benzo[*b*]thiophene, benzo[*b*]furan, indole, pyrrole, selenophene, thiophene, furan, cationic σ-complexes, quantum-chemical calculations, MP2/6-31G(d) and B3LYP/6-31G(d) methods, relative stability of the onium states of chalcogens, positional selectivity, substrate selectivity, electrophilic substitution.

Electrophilic substitution is an important type of reaction for five-membered heterocycles with one heteroatom and enables compounds with various substituents to be obtained. The present work is devoted to a quantum-chemical investigation of certain special features of substrate and positional specificity in the electrophilic substitution of derivatives of pyrrole, furan, thiophene, and selenophene, and also the corresponding benzannelated systems*[2], which had not been explained until recently.

It is well known that the effect of the heteroatom is displayed in an increased reactivity of the α-position, which is usually interpreted as the result of the higher stability of the corresponding σ-complex (**A**) due to better conditions for delocalization of the charge compared with its isomer (**B**) formed on attack at the β-position (Scheme 1).

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* Dedicated to Professor Salo Gronowitz on his 75th birthday.

*[2] For preliminary communications see [1-3].

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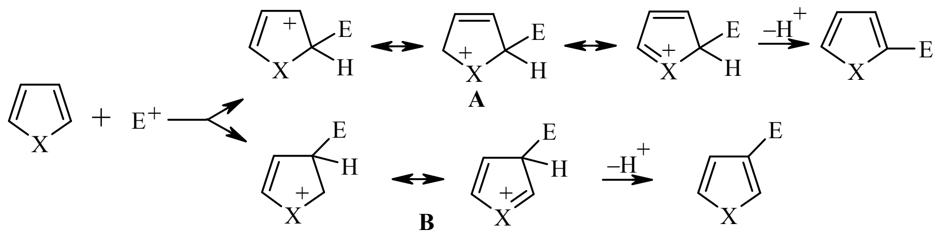
Scheme 1

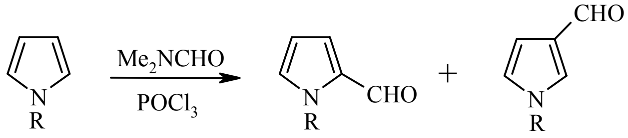


The reactivity and positional selectivity of pyrrole, furan, and thiophene in electrophilic substitution reactions had been studied quantitatively 30 years ago [4,5]. Vast differences are observed in reactivity, which falls by approximately 10 orders of magnitude in the series pyrrole >> furan > thiophene, and may be explained by the different conditions for delocalization of ring atom electron density on ring atoms, in the course of which overlap takes place of the π-orbitals of the C atoms and the *n*-orbitals of the heteroatoms belonging to a different groups and periods of the Periodic System of the elements. The differences in positional selectivity are not so large. For example, on acetylation the difference in α : β ratio (the ratio of products of α- and β-substitution) between the most selective furan and the least selective pyrrole is 'only' three orders of magnitude. It is important to emphasize that this ratio changes in the sequence furan > thiophene > pyrrole, which does not correlate with the reactivity (substrate selectivity) series given above [4,5].

About 20 years ago one of us put forward a hypothesis explaining the reason for the noncorrespondence of the series of substrate and positional selectivities of electrophilic substitution reactions of five-membered heterocycles with one heteroatom [6,7]. The gist of it was that the formation of β-substituted compounds proceeding through a σ-complex of type **B,** in which only the heteroatom and one of the α-carbon atoms participate in charge delocalization, must depend more on the ability of element X to exist in the onium state, than for the formation of α-substituted compounds. In the latter case all the ring atoms except for the geminal C atom participate in charge delocalization of cation **A**. In reality a reduction in the stability of onium states in the series $N^+ > S^+ > O^+$ correllates well with experimental data on the ability of pyrrole, thiophene, and furan to form β-substituted products.

The special features mentioned are also well displayed in the reactions of substituted five-membered heterocycles. It is expedient to begin consideration of such compounds with N-substituted pyrroles, which afford the unique possibility of changing the nature of the heteroatom and the character of its orienting effects (Scheme 2). In the case of N-alkylpyrroles the formation of β-aldehydes on Vilsmeier formylation grows from N-methyl- to N-(*tert*-butyl)pyrrole [8], which might possibly be explained by the growth in steric shielding of

Scheme 2

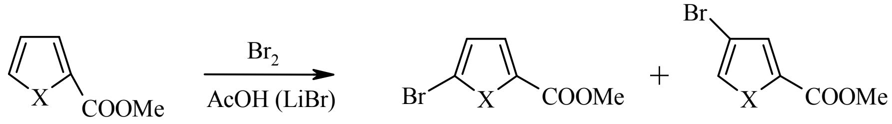


R	α : β	
Me	Only α-isomer	—
Et	11.5	1
i-Pr	1.9	1
t-Bu	1	14
$PhSO_2$	Only α-isomer	—

the position α to the N-alkyl group. However, in the case of N-(benzenesulfonyl)pyrrole, which also contains a bulky substituent at the N atom, the α-aldehyde is formed exclusively [9]. The data given allow one to suggest that the reaction direction in these cases is determined not by steric but by polar factors. An increase in the electron-releasing ability of the N-alkyl group on going from methyl to *tert*-butyl is displayed in an increase in the stabilization of the onium state of the heteroatom and this enables β-substitution (enamine type of electrophilic substitution), while the electron-withdrawing $PhSO_2$ group on the N atom destabilizes the onium state and leads to the formation of only α-substituted derivatives, as observed for derivatives of thiophene and furan.

For compounds carrying electron-withdrawing groups in position 2 there is the possibility of competition between the α-orienting effect of the heteroatom and the *meta* orienting effect of the substituent. The results of this competition are very different for derivatives of pyrrole, thiophene, and furan. The character of these differences may be illustrated by data on the bromination of the corresponding 2-carboxylic acid methyl esters [10] (Scheme 3), in which only 5-bromo derivatives are formed from thiophene and furan esters, but from pyrrole-2-carboxylic ester a mixture is formed in which the 4-bromo substituted ester predominates.

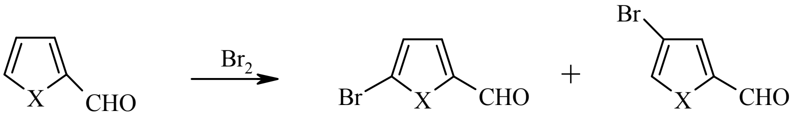
Scheme 3



X	k_{rel} (for position 5)	α : β
NH	5.9×10^8	23:77
O	1.2×10^2	Only α-isomer
S	1.0	Only α-isomer

For aldehydes, which have a stronger electron-withdrawing group, only furfural gives solely the 5-bromo substituted product on bromination in the absence of catalyst [11]. In the case of 2-thiophenecarbaldehyde a small amount of 4-isomer was detected together with 5-bromo-2-thiophenecarbaldehyde [12], but from 2-pyrrolecarbaldehyde the other hand the 4-isomer is formed as almost the sole product and only traces of the 5-bromo substituted product were detected [13]. In addition it must be stressed that N-(*p*-nitrophenyl)-2-pyrrolecarbaldehyde is brominated only at position 5 and this is evidently the result of the electron-withdrawing effect of the N-substituent mentioned above [14] (Scheme 4).

Scheme 4

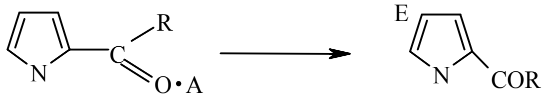


X	Ratio	
	2,5-isomer	2,4-isomer
NH	Traces	Main product
O	Only 2,5-isomer	—
S	97	3
$NC_6H_4NO_2$-*p*	Only 2,5-isomer	—

The orientation on electrophilic substitution of derivatives of pyrrole, thiophene, and furan carrying a substituent of type II orientation at position 2 may be changed by strengthening the electron-withdrawing ability of such substituents by forming complexes with proton and Lewis acids.

Allowing for the abovementioned ability of pyrroles to form β-substituted products it is not surprising that the formation of complexes of strong Lewis acids with practically any 2-RCO substituted compounds of the pyrrole series leads exclusively to the product of electrophilic substitution in position 4 [15-23] (Scheme 5).

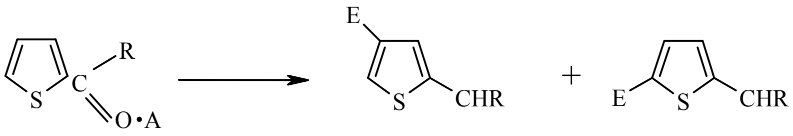
Scheme 5



A = $AlCl_3$, $AlBr_3$, $GaCl_3$, R = Alk, AlkO, AlkS, E = Br, Ac, CHO, Alk

Modification of a substituent by complex formation with aluminum chloride [24-29] or protonation [30-32] enables a high positional selectivity to be achieved in reactions of 2-acylthiophenes. In the mixture of 2,4- and 2,5-substituted products formed the content of the latter did not exceed a few percent (Scheme 6).

Scheme 6

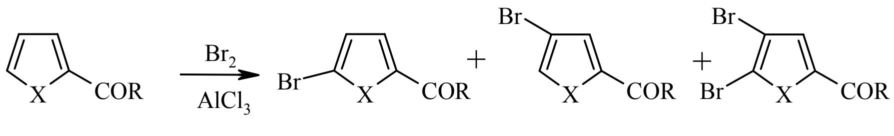


R = H, Me

A	E	2,4- : 2,5-isomer
$AlCl_3$	Br, CH_2Cl, Ac, $ClCH_2CO$	99.5 : 0.5 – 94 : 6
HCl–$SbCl_5$	Br, CH_2Cl, NO_2	98 : 2 – 89 : 11
H_2SO_4	Br, CH_2Cl, NO_2	90 : 10 – 67 : 33

At the same time the synthesis of 4-substituted products from 2-acylfurans and 2-acylselenophenes is an extremely difficult problem. The predominant formation of such compounds was observed on bromination of aluminum chloride complexes of furfural and to a lesser extent of 2-acetylfuran [26]. It was later shown in our collaboration with S. Gronowitz that bromination of complexes of selenophene-2-carbaldehyde and 2-acetylselenophene with $AlCl_3$ leads to the 4-substituted derivative as the main product (the content in the mixture exceeded 70%) [33]. In all cases a significant amount of 4,5-dibromo-substituted products was obtained (Scheme 7). It was established in [33] by competing reactions that the complex of selenophene-2-carbaldehyde with aluminum chloride is brominated more rapidly than its thiophene analog.

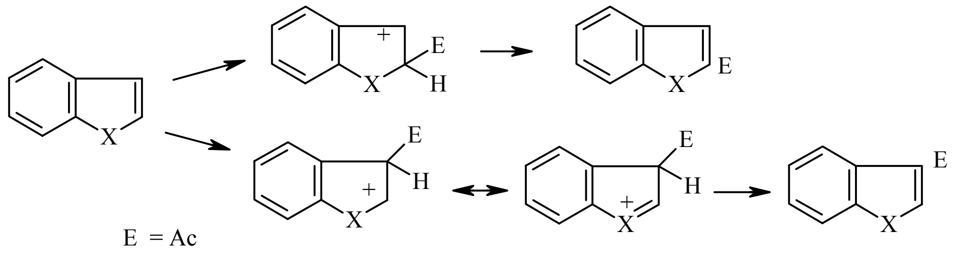
Scheme 7



X	R	Ratio of 5-Br- : 4-Br- : 4,5-Br_2-substituted
O	Me	30 : 30 : 40
O	H	20 : 65 : 15
Se	Me	8 : 73 : 19
Se	H	4 : 86 : 10

The data considered for the first members of the series of five-membered heterocycles confirm the sequence of changes of the relative reactivity (substrate specificity) on electrophilic substitution (pyrrole >> furan > selenophene > thiophene [4,5]) and show that the positional selectivity is reduced in the series furan > selenophene ≥ thiophene > pyrrole, which agrees with that for the relative stability of the onium states of the elements ($O^+ < Se^+ \leq S^+ < N^+$) in agreement with the hypothesis proposed previously [6,7] (however, for a series not including selenophene and its derivatives). Although the quantitative data obtained with the aid of kinetic measurements or by competing reactions are known only for benzothiophene and benzofuran [4,5], it may be assumed that for benzannelated five-membered heterocycles with one heteroatom a sequence of relative reactivity analogous to that given above is retained on electrophilic substitution (indole >> benzo[*b*]furan > benzo[*b*]thiophene), though the position of benzo[*b*]selenophene relative to benzofuran and benzothiophene is difficult to judge. The positional selectivity falls along the series benzo[*b*]furan ≥ benzo[*b*]selenophene > benzo[*b*]thiophene > indole, as indicated by the data on α : β ratios on acetylation [34-36]. These are in agreement with the concept that for delocalization of the positive charge in the nascent σ-complexes (without the participation of the benzene ring and consequently its loss of aromaticity) the attack at the β-position is more preferred then the more stable is the onium state of the ring heteroatom (Scheme 8).

Scheme 8



X	α : β
NH [34]	0 : 100
S [35]	1 : 6
Se [36]	7.0 : 1
O [35]	7.2 : 1

Since there are no quantitative data in the literature on the stability of the onium states (see, for example [37]), and the sequence given above $O^+ < Se^+ \leq S^+ < N^+$ is based on purely qualitative estimates [38-40] arising from the pioneer work of Meerwein [41], we undertook a quantum-chemical investigation of the protonation of monocyclic and the corresponding benzannelated five-membered heterocyclic systems with one heteroatom. The initial calculations, carried out about 20 years ago by the semiempirical CNDO/2 method [42], gave values of the differences in energy of the cations formed on protonation of the α- and β-positions ($\Delta E_{\alpha\text{-}\beta}$), which corresponded with the available experimental data on the sequence of change of positional selectivity furan > thiophene > pyrrole. However, the place of selenophene, between thiophene and pyrrole, in this series predicted by these calculations, was contradicted by results obtained later [33]. The data of calculations by the semiempirical MNDO and PM3 methods were also not adequate to the experimental. This is possibly linked with the special features of parametrization in these methods.

In the present work the assessment of values of $\Delta E_{\alpha\text{-}\beta}$ was carried out using nonempirical quantum-chemical methods (Gaussian 94 set of programs [43]). Calculations were carried out on the 6-31G(d) basis [RHF/6-31G(d)] by the methods of MP2/6-31G (calculation of the correlation of electrons according to second order perturbation theory) with the geometry preliminarily calculated by the method of RHF/6-31D(d) and B3LYP/6-31G using a hybrid functional with complete optimization of the geometry. The main results are given in Table 1. The values of $\Delta E_{\alpha\text{-}\beta}$ obtained by all three methods qualitatively correctly reflect the dependencies of

TABLE 1. Total Energies of Five-membered Heterocycles with One Heteroatom (E_{tot}), Differences in Energies of Cationic σ-Complexes Formed on Protonation, and of the Neutral Molecules for the α- (ΔE_{α}, kcal/mol) and β-Positions (ΔE_{β}, kcal/mol), and also Values of $\Delta E_{\alpha\text{-}\beta}$, kcal/mol = $\Delta E_{\alpha} - \Delta E_{\beta}$

Molecule (cation)	RHF/6-31G(d)//RHF/6-31G(d)				MP2/6-31G(d)//RHF/6-31G(d)				B3LYP/6-31G(d)//B3LYP/6-31G(d)			
	$E_{0tot.}$, a. u.*	ΔE_{α},	ΔE_{β}	$\Delta E_{\alpha-\beta}$	$E_{tot.}$, a. u.*	ΔE_{α}	ΔE_{β}	$\Delta E_{\alpha-\beta}$	$E_{0tot.}$, a. u.*	ΔE_{α}	ΔE_{β}	$\Delta E_{\alpha-\beta}$
Pyrrole	-208.7286	-222.00	-214.54	-7.6	-209.3985	-209.01	-204.02	-5.0	-210.0865	-214.74	-209.12	-5.6
Furan	-228.5576	-206.96	-193.83	-13.1	-229.2399	-193.24	-181.42	-11.8	-229.9531	-200.75	-188.46	-12.3
Thiophene	-551.2260	-202.56	-191.14	-11.4	-551.8585	-194.02	-185.50	-8.5	-552.9383	-201.08	-190.82	-10.3
Selenophene	-2551.2847	-205.29	-192.57	-12.7	-2551.9056	-196.69	-187.01	-9.7	-2554.1219	-205.13	-193.53	-11.6
Indole	-361.3434	-218.28	-222.69	4.4	-362.5152	-202.90	-212.99	10.1	-363.6918	-213.31	-218.00	4.7
Benzo[*b*]furan	-381.1753	-218.06	-201.23	-16.8	-382.3574	-202.43	-190.72	-11.7	-383.5603	-204.95	-197.61	-7.3
Benzo[*b*]thiophene	-703.8418	-206.31	-198.90	-7.4	-704.9763	-192.82	-192.08	-0.7	-706.5437	-205.31	-199.79	-5.5
Benzo[*b*]selenophene	-2703.9041	-208.68	-198.86	-9.8	-2705.0273	-196.84	-186.34	-10.5	-2707.7308	-208.54	-202.43	-6.1

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* The energies are given with a ZPE (zero-point energy correction) to the difference of energies at the minimum of the potential energy surface and the first vibrational level obtained from the formula $E_0 = E_{calc} + k \cdot \text{ZPE}$. The values of the ZPE were found on calculating the appropriate vibrational spectra. Normalized factors *k* were used equal to 0.8929 (RHF/6-31G, MP2/6-31G) and 0.9613 (B3LYP/6-31G) [45].

TABLE 2. Geometry [RHF/6-31G(d)] of the Pyrrole, Furan and Selenophene Molecules (the Experimental Data of [44] are Given in Parentheses) and of the 2H- and 3H-Hetarenium Ions Formed by Them

Molecule (cation)	*d*, Å								ω, deg.					
	$X_{(1)}–C_{(2)}$	$X_{(1)}–C_{(5)}$	$C_{(2)}–C_{(3)}$	$C_{(3)}–C_{(4)}$	$C_{(4)}–C_{(5)}$	$C_{(sp3)}–H$	$C_{(sp2)}–H$	N–H	$C_{(2)}X_{(1)}C_{(5)}$	$X_{(1)}C_{(2)}C_{(3)}$	$C_{(2)}C_{(3)}C_{(4)}$	$C_{(3)}C_{(4)}C_{(5)}$	$C_{(4)}C_{(5)}X_{(1)}$	$HC_{(sp3)}H$
Pyrrole	1.36 (1.37)	1.36 (1.37)	1.36 (1.38)	1.43 (1.42)	1.36 (1.38)	—	1.07 (1.08)	1.07	109.5 (109.8)	108.2 (107.7)	107.1 (107.4)	107.1 (107.4)	108.2 (107.7)	—
Furan	1.34 (1.36)	1.34 (1.36)	1.34 (1.36)	1.44 (1.43)	1.34 (1.36)	—	1.07 (1.08)	—	107.1 (106.5)	110.8 (110.7)	105.6 (106.1)	105.6 (106.1)	110.8 (110.7)	—
Thiophene	1.73 (1.71)	1.73 (1.71)	1.35 (1.37)	1.44 (1.43)	1.35 (1.37)	—	1.07 (1.08)	—	91.3 (92.2)	111.8 (111.5)	112.5 (112.5)	112.5 (112.5)	111.8 (111.5)	—
Selenophene	1.86 (1.86)	1.86 (1.86)	1.34 (1.37)	1.44 (1.43)	1.34 (1.37)	—	1.07 (1.07-1.08)	—	87.3 (87.8)	111.7 (111.6)	114.7 (114.6)	114.7 (114.6)	111.7 (111.6)	—
2H-Pyrrolium	1.46	1.29	1.49	1.34	1.44	1.084	1.070-1.074	1.00	111.1	101.2	110.3	106.5	110.8	109.0
2H-Furanium	1.44	1.26	1.49	1.34	1.42	1.082	1.070-1.075	—	109.3	102.7	109.3	105.1	113.7	110.1
2H-Thiophenium	1.81	1.66	1.48	1.35	1.42	1.086	1.072-1.076	—	91.6	106.0	115.2	111.2	115.9	107.9
2H-Selenophenium	1.94	1.79	1.48	1.35	1.41	1.085	1.072-1.075	—	87.7	105.9	117.3	113.2	115.9	108.7
3H-Pyrrolium	1.27	1.44	1.49	1.50	1.32	1.088	1.069-1.073	1.00	111.8	109.3	101.7	109.1	108.0	106.9
3H-Furanium	1.24	1.43	1.48	1.50	1.31	1.089	1.067-1.076	—	109.8	112.2	100.2	108.6	109.2	106.9
3H-Thiophenium	1.62	1.77	1.48	1.50	1.32	1.091	1.071-1.075	—	93.3	114.1	106.6	114.4	111.6	105.8
3H-Selenophenium	1.75	1.91	1.48	1.50	1.32	1.091	1.071-1.075	—	89.3	114.3	108.6	116.6	111.3	105.5

TABLE 3. Geometry [RHF/6-31G(d)] of the Indole, Benzo[*b*]furan, Benzo[*b*]thiophene, and Benzo[*b*]selenophene Molecules and of the 2H- and 3H-Hetarenium Ions Formed by Them

Molecule (cation)	*d*, Å												
	$X_{(1)}–C_{(2)}$	$X_{(1)}–C_{(7a)}$	$C_{(2)}–C_{(3)}$	$C_{(3)}–C_{(3a)}$	$C_{(3a)}–C_{(4)}$	$C_{(4)}–C_{(5)}$	$C_{(5)}–C_{(6)}$	$C_{(6)}–C_{(7)}$	$C_{(7)}–C_{(7a)}$	$C_{(3a)}–C_{(7a)}$	$C_{(sp3)}–H$	$C_{(sp2)}–H$	N–H
Indole	1.37	1.37	1.35	1.44	1.40	1.37	1.40	1.37	1.39	1.40	—	1.07	0.99
Benzo[*b*]furan	1.35	1.35	1.33	1.45	1.39	1.38	1.40	1.38	1.38	1.39	—	1.07	—
Benzo[*b*]thiophene	1.74	1.75	1.33	1.45	1.40	1.37	1.40	1.38	1.39	1.40	—	1.07-1.08	—
Benzo[*b*]selenophene	1.87	1.88	1.33	1.45	1.40	1.38	1.40	1.38	1.39	1.40	—	1.07-1.08	—
2H-Indolium	1.45	1.31	1.49	1.34	1.45	1.34	1.45	1.35	1.42	1.45	1.085	1.07	1.00
2H-Benzo[*b*]furanium	1.42	1.29	1.49	1.35	1.44	1.34	1.44	1.37	1.40	1.44	1.083	1.075	—
2H-Benzo[*b*]thiophenium	1.81	1.72	1.48	1.35	1.44	1.35	1.43	1.37	1.39	1.44	1.086	1.075	—
2H-Benzo[*b*]selenophenium	1.95	1.85	1.48	1.36	1.44	1.35	1.43	1.38	1.39	1.44	1.084	1.075	—
3H-Indolium	1.27	1.43	1.50	1.51	1.38	1.39	1.39	1.39	1.37	1.38	1.087	1.074	1.00
3H-Benzo[*b*]furanium	1.24	1.43	1.49	1.51	1.38	1.39	1.39	1.39	1.37	1.37	1.089	1.075	—
3H-Benzo[*b*]thiophenium	1.62	1.77	1.49	1.50	1.38	1.39	1.39	1.38	1.38	1.39	1.090	1.075	—
3H-Benzo[*b*]selenophenium	1.75	1.90	1.47	1.50	1.38	1.39	1.39	1.38	1.38	1.39	1.090	1.075	—

Molecule (cation)	ω, deg					
	$C_{(2)}X_{(1)}C_{(7a)}$	$X_{(1)}C_{(2)}C_{(3)}$	$C_{(2)}C_{(3)}C_{(3a)}$	$C_{(3)}C_{(3a)}C_{(7a)}$	$C_{(3a)}C_{(7a)}X_{(1)}$	$HC_{(sp3)}H$
Indole	109.0	110.0	106.7	106.7	107.5	—
Benzo[*b*]furan	106.5	112.6	105.5	104.9	110.4	—
Benzo[*b*]thiophene	90.8	113.4	112.8	111.8	111.2	—
Benzo[*b*]selenophene	87.0	113.0	115.1	113.8	111.09	—
2H-Indolium	111.4	102.1	109.9	107.2	109.4	108.5
2H-Benzo[*b*]furanium	109.2	104.0	108.7	105.8	112.2	109.4
2H-Benzo[*b*]thiophenium	91.8	106.9	115.6	112.2	113.5	107.7
2H-Benzo[*b*]selenophenium	88.0	106.8	117.7	114.2	113.3	108.5
3H-Indolium	112.2	110.8	101.4	108.5	107.1	107.2
3H-Benzo[*b*]furanium	109.9	113.8	100.0	107.6	108.7	107.0
3H-Benzo[*b*]thiophenium	93.8	115.5	106.5	113.3	110.9	106.2
3H-Benzo[*b*]selenophenium	89.9	115.5	108.5	115.4	110.7	106.0

TABLE 4. Charges on Atoms according to Mulliken Calculated by the MP2/6-31G(d) Method for the Molecules of Pyrrole, Furan, Thiophene, Selenophene and of the 2H- and 3H-Hetarenium Ions Formed by Them

Molecule (cation)	$X_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$H_{(1)}$	$H_{(2)}$	$H_{(3)}$	$H_{(4)}$	$H_{(5)}$
Pyrrole	-0.535	-0.086	-0.322	-0.322	-0.086	0.427	0.227	0.237	0.237	0.227
Furan	-0.437	0.087	-0.335	-0.335	0.087	—	0.222	0.245	0.245	0.222
Thiophene	0.455	-0.446	-0.281	-0.281	-0.446	—	0.255	0.244	0.244	0.255
Selenophene	0.525	-0.482	-0.280	-0.280	-0.482	—	0.256	0.244	0.244	0.256
2H-Pyrrolium	-0.439	-0.325	-0.105	-0.274	0.183	0.476	0.313	0.285	0.293	0.280
2H-Furanium	-0.346	-0.173	-0.071	-0.307	0.400	—	0.312	0.294	0.304	0.275
2H-Thiophenium	0.730	-0.686	-0.058	-0.253	-0.298	—	0.337	0.288	0.300	0.305
2H-Selenophenium	0.862	-0.730	-0.063	-0.252	-0.372	—	0.334	0.285	0.299	0.303
3H-Pyrrolium	-0.421	0.226	-0.580	-0.158	-0.063	0.478	0.279	0.334	0.289	0.281
3H-Furanium	-0.312	0.486	-0.618	-0.200	0.090	—	0.273	0.347	0.302	0.284
3H-Thiophenium	0.834	-0.288	-0.581	-0.138	-0.417	—	0.306	0.345	0.293	0.301
3H-Selenophenium	0.983	-0.373	-0.581	-0.147	-0.461	—	0.303	0.342	0.292	0.300

TABLE 5. Charges on Atoms According to Mulliken Calculated by the MP2-6-31G(d) Method for the Molecules of Indole, Benzo[*b*]furan, Benzo[*b*]thiophene, Benzo[*b*]selenophene, and of the 2H- and 3H-Hetarenium Ions Formed by Them

Molecule (cation)	$X_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(3a)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(7a)}$	$H_{(1)}$	$H_{(2)}$	$H_{(3)}$	$H_{(4)}$	$H_{(5)}$	$H_{(6)}$	$H_{(7)}$
Indole	-0.695	0.021	-0.236	0.021	-0.201	-0.181	-0.196	-0.182	0.261	0.166	0.176	0.367	0.184	0.168	0.163	0.163
Benzo[*b*]furan	-0.469	0.066	-0.235	0.017	-0.199	-0.180	-0.188	-0.204	0.289	—	0.197	0.194	0.176	0.171	0.173	0.190
Benzo[*b*]thiophene	0.695	-0.382	-0.137	0.060	-0.179	-0.184	-0.167	-0.181	-0.189	—	0.201	0.186	0.175	0.173	0.174	0.184
Benzo[*b*]selenophene	0.073	-0.281	-0.142	0.045	-0.183	-0.181	-0.170	0.187	0.045	—	0.203	0.184	0.176	0.174	0.175	0.183
2H-Indolium	-0.481	-0.316	-0.061	-0.100	-0.185	-0.198	-0.125	-0.260	0.287	0.463	0.307	0.277	0.269	0.272	0.269	0.273
2H-Benzo[*b*]furanium	-0.400	-0.161	-0.027	-0.136	-0.171	-0.197	-0.101	-0.268	-0.136	—	0.300	0.283	0.273	0.278	0.274	0.290
2H-Benzo[*b*]thiophenium	0.574	-0.676	0.008	-0.103	-0.162	-0.191	-0.110	-0.225	-0.147	—	0.328	0.278	0.270	0.277	0.272	0.281
2H-Benzo[*b*]selenophenium	0.680	-0.724	0.012	-0.105	-0.158	-0.191	-0.111	-0.224	-0.204	—	0.327	0.275	0.269	0.276	0.271	0.279
3H-Indolium	-0.396	0.274	0.321	-0.040	-0.199	-0.182	-0.198	-0.221	0.097	0.474	0.274	0.321	0.265	0.266	0.267	0.265
3H-Benzo[*b*]furanium	-0.292	0.489	-0.586	-0.081	-0.193	-0.183	-0.192	-0.231	0.241	—	0.267	0.334	0.269	0.269	0.272	0.283
3H-Benzo[*b*]thiophenium	0.859	-0.288	-0.546	-0.036	-0.196	-0.176	-0.192	-0.212	-0.246	—	0.301	0.330	0.266	0.267	0.270	0.269
3H-Benzo[*b*]selenophenium	1.009	-0.370	-0.547	-0.040	-0.197	-0.178	-0.192	-0.218	-0.289	—	0.299	0.328	0.264	0.266	0.268	0.267

positional selectivity, experimentally observed on electrophilic substitution, on the structure of the heteroaromatic compound as furan > selenophene > thiophene > pyrrole and benzo[*b*]furan > benzo[*b*]selenophene > benzo[*b*]thiophene > indole. Special attention should be paid to the change in sign of the value of $\Delta E_{\alpha\text{-}\beta}$ in the case of indole, which reflects the higher reactivity of its β-position compared with the α-position (α-substituted products are not detected in practice in reactions of indole with electrophiles).

The geometric characteristics (Tables 2 and 3) of the systems studied calculated by the RHF/6-31G method are in good agreement with the experimental data for neutral molecules, which are summarized in Katritzky and Pozharskii's book [44], and are given in Table 2 in parentheses for pyrrole, furan, thiophene, and selenophene. On going over from the neutral molecule to the cation in the case of 2H-hetarenium ions the bonds $X_{(1)}$–$C_{(2)}$, $C_{(2)}$–$C_{(3)}$, and $C_{(4)}$–$C_{(5)}$ in the monocyclic and $X_{(1)}$–$C_{(2)}$, $C_{(2)}$–$C_{(3)}$, $C_{(3a)}$–$C_{(4)}$, $C_{(5)}$–$C_{(6)}$, and $C_{(3a)}$–$C_{(7a)}$ in the bicyclic ions are lengthened. On the other hand the bonds $X_{(1)}$–$C_{(5)}$ and $C_{(3)}$–$C_{(4)}$ in the mono and $X_{(1)}$–$C_{(7a)}$ and $C_{(3)}$–$C_{(3a)}$ in the bicyclic ions are shortened. In the case of the 3H-hetarenium ions the bonds $X_{(1)}$–$C_{(2)}$, and $C_{(4)}$–$C_{(5)}$ in the monocyclic and $X_{(1)}$–$C_{(2)}$ in the bicyclic ions were shortened but the bonds $X_{(1)}$–$C_{(5)}$, $C_{(2)}$–$C_{(3)}$, and $C_{(3)}$–$C_{(4)}$ in the monocyclic and $X_{(1)}$–$C_{(7a)}$, $C_{(2)}$–$C_{(3)}$, and $C_{(3)}$–$C_{(3a)}$ in the bicyclic ions were lengthened. This clearly reflects the changes in their multiplicity on going from a neutral molecule to a σ-complex. It is interesting to note that in difference to the bicyclic 2H-hetarenium ions the C–C bond lengths in the benzene rings in their 3H isomers were changed far less compared with the corresponding values in the neutral molecules and differed less between themselves. All the values were contained within the range 1.37-1.39 Å characteristic of compounds in the benzene series. This special feature, in our opinion, indicates that in the case of bicyclic 3H-hetarenium ions the benzene ring does not participate in practice in the delocalization of the positive charge, which is effected fairly efficiently in the five-membered ring with the participation of the heteroatom and the $C_{(2)}$ atom (see Scheme 8).

The charges on the atoms calculated according to Mulliken (Tables 4 and 5) do not give a clear reflection of the changes in electron density on going from the neutral molecule to the cation, which affects the π-system first of all. In particular, the charges on the heteroatoms seemingly depend mainly on the electronegativity of the corresponding elements, although the character of the change in charge on going from a neutral molecule to a cation corresponds to that expected from a chemical point of view. To clarify the rules of the changes indicated we intend subsequently to carry out a quantum chemical investigation of nonaromatic models both including and not including C=X double bonds.

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