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QUANTUM-CHEMICAL STUDY OF THE PROTONATION MECHANISM OF *p*-FLUORSTYROL BY THE MNDO METHOD

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Abstract: The mechanism of protonation of *p*-fluorstyrol first studied by classical quantum-chemical method MNDO. This mechanism is a reaction of the electrophilic addition of a proton to the double bond of a monomer. The reaction is exothermic and has no barrier character. The gain of energy as a result of the reaction in the attack on the α-carbon atom is -540 kJ/mol. The reaction follows the classical scheme in accordance with Markovnikov rule.
Keywords: protonation mechanism, MNDO method, *p*-fluorostyrene, Markovnikov rule.

Study of the mechanism of protonation of *p*-fluorstyrol [1] is the first step in the study of the mechanism of cationic polymerization of this monomer. The aim of the present work is a quantum-chemical study of the mechanism of protonation of *p*-fluorstyrol by classical semi-empirical method MNDO.

Methodical Part

The methodology for studying the protonation mechanism of *p*-fluorostyrene is completely consistent with the method used to study the mechanism for the protonation of p-ethylstyrene [2-4]. 17 Atoms are in the system H^+ ... C_8H_7F. M = 2S + 1 = 1 (S is the total spin of all electrons of the system under study is equal to zero. All electrons are paired. M-multiplicity). The total charge of the molecular system is $\sum q_c = 1$. The reaction coordinates were the distances from the proton H_1 to C_2 (RH_1C_2) and from H_1 to C_3 (RH_1C_3). The equipotential surface of the interactions of the proton with the p-fluorosterene was constructed according to the data obtained, the energy values along the reaction coordinates (Fig. 4.). The initial model of the proton attack of the p-fluorostyrene molecule is shown in Fig. 1.

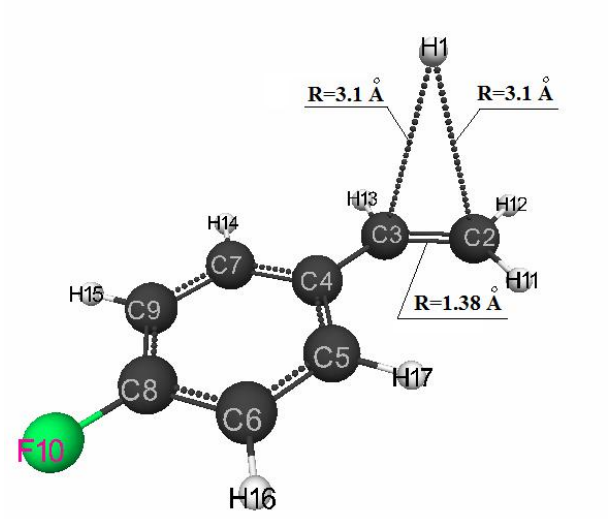

Fig. 1. *The initial model of the attack of proton of the molecule p-fluorothyrene.*

For the visual presentation of molecular models was used the well-known program MacMolPlt [5].

Results and Discussion

The structure of the formed carbocation (I) after the attack of the proton H_1 of the α – carbon atom of *p*-fluorostyrene (C_2) and the rupture of the double bond of *p*-fluorothyrene is shown in Fig. 2. The structure of the formed carbocation (II) after the attack of the proton H1 β – carbon atom of *p*-fluorostyrene (C_3) and the breaking of the double bond $C_2 = C_3$ is shown in Fig. 3. The charges on the carbocation atoms (I) and (II) are presented in Table. 1. The change in total energy during protonation of *p*-fluorostyrene is shown in Fig. 4. Negative values of the total energy of the system H^+ ... C_8H_7F (E_0) increases along the entire path of motion of the initiating particle H^+ along the coordinates of the reaction RH_1C_2 and RH_1C_3. The energy barrier is absent both when attacking α- and β-carbon atoms of *p*-fluorostyrene. Structure (I) at 68 kJ/mol is energetically more favorable

than (II). This is in full accordance with the classical Markovnikov rule. The energy gain due to the formation of (I) is 540 kJ/mol, and during the formation of (II) 472 kJ/mol.

Analysis of the results of quantum chemical calculations, the changes of bond lengths and valence angles along the reaction coordinate during the attack of the proton on the α- and β-carbon atoms of a *p*-fluorostyrene suggests that the mechanism of protonation of the cationic polymerization of *p*-fluorostyrene goes according to the classical scheme of addition of the proton to the double bond of the monomer.

Thus, we first studied the mechanism of protonation of *p*-fluorostyrene quantum-chemical method MNDO. It is shown that this mechanism is a usual reaction of the proton addition to the olefin double bond. The reaction is exothermic and barrier-free. The reactions are energetically advantageous to follow the classical scheme in accordance with the Markovnikov rule.

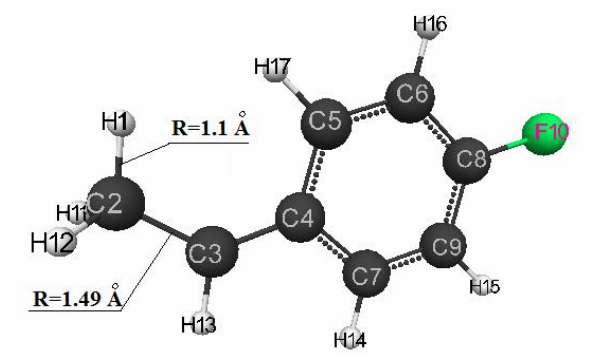

***Fig.2**. The structure of the formed carbocation (I) after the attack of the proton H_1 of the α - carbon atom of p-fluorostyrene (C_2)*

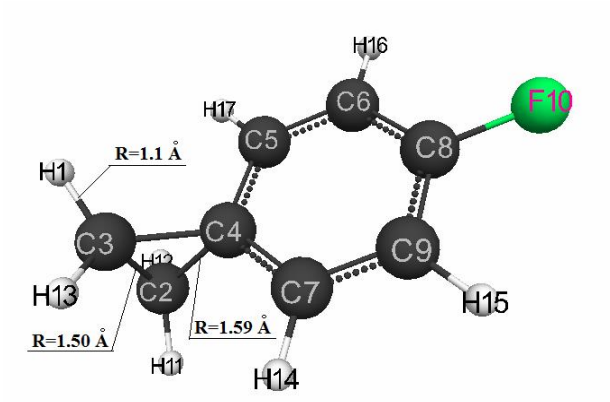

***Fig.3.** - The structure of the formed carbocation (II) after the attack of the proton H_1 of the β– carbon atom of p-fluorostyrene (C_3)*

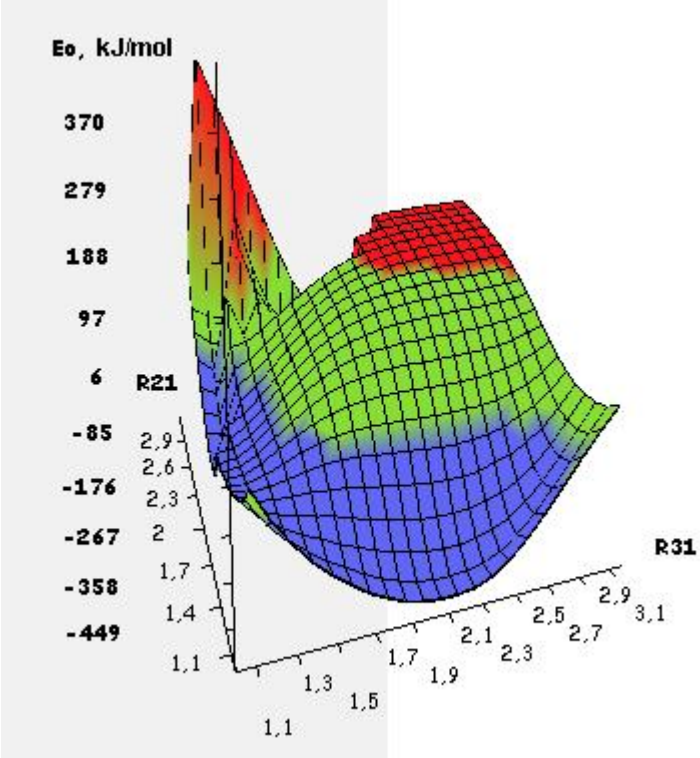

Fig. 4. *Potential surface of the energy of the interactions of the proton with p-fluorostyrene*

Fig. 5. *The change in total energy at the accession of the proton H_1 to the α–carbon atom of p-fluorostyrene*

Table 1. *Changes in bond lengths along the path of the H_1 proton addition reaction to the α-carbon atom of a p-fluorostyrene*

Step number	1	2	3	4	5	6	7	8	9	10
C(2)-H(1)	3,10	3,00	2,90	2,80	2,70	2,60	2,50	2,40	2,30	2,20
C(3)-H(1)	3,10	3,00	3,00	3,00	2,90	2,90	2,90	2,80	2,80	2,70
C(3)-C(2)	1,38	1,38	1,38	1,39	1,39	1,39	1,40	1,40	1,41	1,41

C(4)-C(3)	1,44	1,44	1,44	1,44	1,44	1,43	1,43	1,43	1,43	1,42
C(5)-C(4)	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44
C(6)-C(5)	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39
C(7)-C(4)	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44
C(8)-C(9)	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43
C(8)-C(6)	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43
C(9)-C(7)	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39
F(10)-C(8)	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31
H(11)-C(2)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(12)-C(2)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(13)-C(3)	1,10	1,10	1,10	1,10	1,10	1,10	1,10	1,10	1,10	1,10
H(14)-C(7)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(15)-C(9)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(16)-C(6)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(17)-C(5)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09

Continuation of ***table 1***

Step number	11	12	13	14	15	16	17	18	19	20	21
C(2)-H(1)	2,10	2,00	1,90	1,80	1,70	1,60	1,50	1,40	1,30	1,20	1,10
C(3)-H(1)	2,70	2,60	2,60	2,60	2,50	2,50	2,50	2,40	2,40	2,30	2,20
C(3)-C(2)	1,42	1,43	1,43	1,45	1,45	1,46	1,48	1,48	1,49	1,49	1,49
C(4)-C(3)	1,42	1,42	1,41	1,41	1,41	1,40	1,40	1,40	1,39	1,39	1,39
C(5)-C(4)	1,44	1,44	1,45	1,45	1,45	1,45	1,45	1,45	1,45	1,45	1,45
C(6)-C(5)	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39
C(7)-C(4)	1,45	1,45	1,45	1,45	1,45	1,45	1,46	1,46	1,46	1,46	1,46
C(8)-C(9)	1,43	1,43	1,43	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44
C(8)-C(6)	1,43	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44
C(9)-C(7)	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39
F(10)-C(8)	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31
H(11)-C(2)	1,09	1,09	1,09	1,09	1,09	1,10	1,10	1,10	1,11	1,11	1,11
H(12)-C(2)	1,09	1,09	1,09	1,09	1,09	1,09	1,10	1,10	1,11	1,11	1,11
H(13)-C(3)	1,10	1,10	1,10	1,10	1,10	1,10	1,10	1,10	1,10	1,10	1,10
H(14)-C(7)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(15)-C(9)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(16)-C(6)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(17)-C(5)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09

Table 2*. Changes in the valence angles along the reaction path for the addition of the proton H_1 to the α – carbon atom of p-fluorostyrene*

step number	1	2	3	4	5	6	7	8	9	10
C(3)-C(2)-H(1)	77	77	80	84	84	88	92	91	95	94
C(2)-C(3)-H(1)	77	77	72	68	68	64	60	59	55	54
C(4)-C(3)-C(2)	129	129	129	129	129	129	129	129	129	129
C(5)-C(4)-C(3)	124	124	124	124	124	124	124	124	124	124
C(6)-C(5)-C(4)	122	122	122	122	122	122	122	122	122	122
C(7)-C(4)-C(3)	119	119	119	119	119	119	119	119	119	119
C(8)-C(9)-C(7)	120	120	120	120	120	120	120	120	120	120
C(8)-C(6)-C(5)	120	120	120	120	120	120	120	120	120	120
C(9)-C(7)-C(4)	122	122	122	122	122	122	122	122	122	122
F(10)-C(8)-C(9)	120	120	120	120	120	120	120	120	120	120
H(11)-C(2)-C(4)	99	99	99	99	99	99	99	99	99	98
H(12)-C(2)-C(4)	147	147	147	147	147	146	146	146	145	145
H(13)-C(3)-C(2)	116	116	115	115	115	115	115	115	115	115
H(14)-C(7)-C(4)	120	120	120	120	120	120	120	120	120	120
H(15)-C(9)-C(7)	120	120	120	120	120	120	120	120	120	120
H(16)-C(6)-C(5)	120	120	120	120	120	120	120	120	120	120
H(17)-C(5)-C(4)	120	120	120	120	120	120	120	120	120	120

Continuation of ***table 2***

Step number	11	12	13	14	15	16	17	18	19	20	21
C(3)-C(2)-H(1)	98	97	102	106	105	109	114	113	118	117	115
C(2)-C(3)-H(1)	50	50	46	42	41	37	33	33	28	28	27
C(4)-C(3)-C(2)	129	129	129	129	129	129	129	129	130	130	130
C(5)-C(4)-C(3)	124	124	124	124	124	124	124	124	124	124	124
C(6)-C(5)-C(4)	122	122	122	122	122	122	122	122	122	122	122
C(7)-C(4)-C(3)	119	119	119	119	119	119	120	120	119	119	119
C(8)-C(9)-C(7)	120	120	120	120	120	120	120	120	120	120	120
C(8)-C(6)-C(5)	120	120	120	120	120	120	120	120	120	120	120
C(9)-C(7)-C(4)	122	122	122	122	122	122	122	122	122	122	122
F(10)-C(8)-C(9)	120	120	120	120	120	120	120	120	120	120	120
H(11)-C(2)-C(4)	98	98	97	97	96	138	137	136	121	120	120
H(12)-C(2)-C(4)	144	143	142	140	139	95	95	95	119	120	120
H(13)-C(3)-C(2)	114	114	114	114	114	113	113	113	112	112	112
H(14)-C(7)-C(4)	119	119	119	119	119	119	119	119	119	119	119
H(15)-C(9)-C(7)	120	120	120	120	120	120	120	120	120	120	120
H(16)-C(6)-C(5)	120	120	120	120	120	120	120	120	120	120	120
H(17)-C(5)-C(4)	120	120	120	120	120	120	120	120	120	120	120

Table 3. *Changes in charges along the path of the proton H_1 addition reaction to the α – carbon atom of p-fluorostyrene*

Atom	1	2	3	4	5	6	7	8	9	10
H(1)	0,388	0,377	0,369	0,360	0,344	0,332	0,318	0,296	0,279	0,254
C(2)	0,059	0,061	0,048	0,033	0,032	0,015	-0,003	-0,007	-0,028	-0,032
C(3)	-0,011	-0,002	0,016	0,037	0,050	0,074	0,099	0,117	0,144	0,163
C(4)	-0,102	-0,111	-0,119	-0,128	-0,138	-0,148	-0,158	-0,169	-0,179	-0,190
C(5)	0,032	0,037	0,041	0,046	0,051	0,058	0,065	0,071	0,079	0,086
C(6)	-0,108	-0,109	-0,112	-0,114	-0,116	-0,118	-0,122	-0,124	-0,127	-0,130
C(7)	0,048	0,051	0,056	0,062	0,066	0,072	0,078	0,083	0,090	0,096
C(8)	0,288	0,290	0,293	0,297	0,300	0,304	0,309	0,314	0,320	0,326
C(9)	-0,111	-0,113	-0,114	-0,116	-0,118	-0,121	-0,123	-0,126	-0,129	-0,132
F(10)	-0,124	-0,124	-0,124	-0,124	-0,124	-0,123	-0,122	-0,121	-0,120	-0,118
H(11)	0,075	0,077	0,077	0,077	0,079	0,080	0,080	0,082	0,082	0,083
H(12)	0,081	0,082	0,083	0,083	0,085	0,086	0,086	0,088	0,088	0,090
H(13)	0,082	0,082	0,083	0,084	0,084	0,084	0,085	0,086	0,086	0,086
H(14)	0,089	0,089	0,089	0,089	0,089	0,090	0,090	0,090	0,091	0,092
H(15)	0,117	0,117	0,117	0,118	0,118	0,118	0,119	0,120	0,121	0,122
H(16)	0,115	0,115	0,116	0,116	0,116	0,117	0,118	0,118	0,119	0,120
H(17)	0,081	0,081	0,080	0,080	0,080	0,081	0,081	0,082	0,083	0,084

Continuation of ***table 3***

Atom	11	12	13	14	15	16	17	18	19	20	21
H(1)	0,234	0,207	0,187	0,169	0,145	0,132	0,120	0,103	0,053	0,048	0,042
C(2)	-0,053	-0,056	-0,074	-0,086	-0,081	-0,083	-0,080	-0,066	-0,049	-0,036	-0,023
C(3)	0,191	0,208	0,232	0,250	0,258	0,268	0,273	0,272	0,270	0,265	0,261
C(4)	-0,199	-0,208	-0,214	-0,219	-0,224	-0,226	-0,227	-0,228	-0,226	-0,226	-0,226
C(5)	0,095	0,102	0,111	0,120	0,126	0,132	0,136	0,139	0,146	0,146	0,145
C(6)	-0,134	-0,137	-0,141	-0,145	-0,148	-0,151	-0,153	-0,154	-0,158	-0,157	-0,157
C(7)	0,103	0,109	0,116	0,122	0,126	0,131	0,135	0,138	0,139	0,139	0,139
C(8)	0,334	0,341	0,350	0,359	0,366	0,373	0,379	0,383	0,388	0,388	0,388
C(9)	-0,136	-0,138	-0,142	-0,146	-0,148	-0,151	-0,154	-0,155	-0,156	-0,156	-0,156
F(10)	-0,116	-0,114	-0,112	-0,110	-0,108	-0,106	-0,104	-0,103	-0,101	-0,101	-0,101
H(11)	0,082	0,082	0,079	0,075	0,072	0,077	0,069	0,066	0,072	0,071	0,070
H(12)	0,090	0,091	0,089	0,085	0,083	0,067	0,062	0,060	0,073	0,071	0,070
H(13)	0,086	0,087	0,086	0,086	0,087	0,087	0,088	0,088	0,088	0,087	0,086
H(14)	0,093	0,094	0,095	0,096	0,097	0,098	0,100	0,100	0,101	0,100	0,100

H(15)	0,123	0,124	0,125	0,126	0,127	0,128	0,129	0,130	0,131	0,131	0,131
H(16)	0,121	0,122	0,124	0,125	0,126	0,128	0,129	0,129	0,130	0,130	0,130
H(17)	0,086	0,087	0,090	0,092	0,094	0,096	0,097	0,098	0,100	0,100	0,100

Fig. 6. *Change of charges on some atoms when the proton H_1 is attached to the α – carbon atom of p-fluorostyrene*

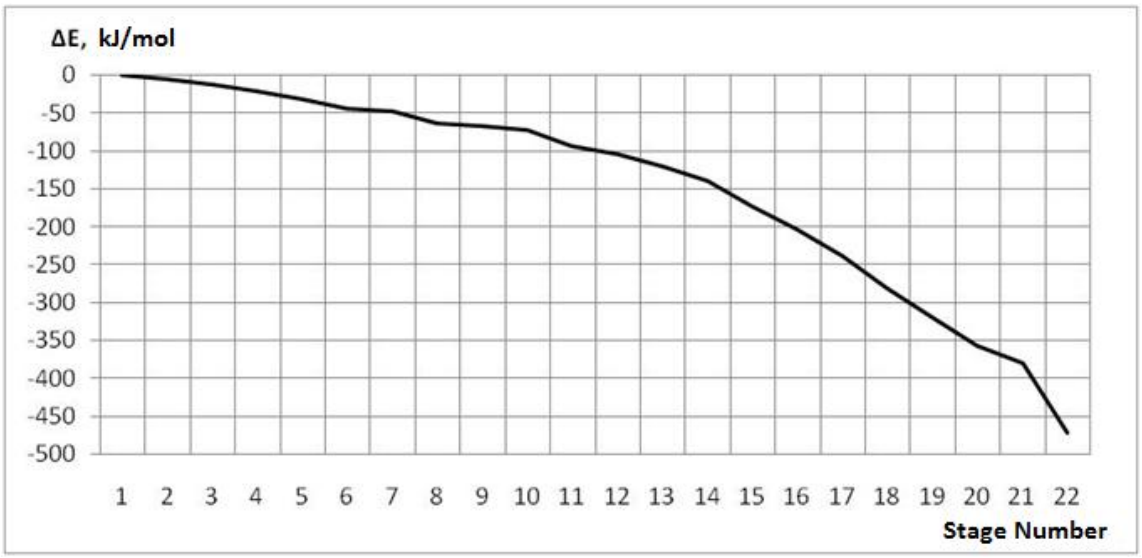

Fig. 7. *The change in total energy when the proton H_1 is attached to the β – carbon atom of p-fluoropyrene*

Table 4. *Change in bond lengths when the proton H_1 is attached to the β – carbon atom of p-fluoropyrene*

Step number	1	2	3	4	5	6	7	8	9	10	11
C(2)-H(1)	3,10	3,00	2,90	2,80	2,70	2,60	2,60	2,50	2,50	2,50	2,40
C(3)-H(1)	3,10	3,10	3,00	2,90	2,80	2,70	2,60	2,50	2,40	2,30	2,20
C(2)-C(4)	2,54	2,55	2,55	2,55	2,55	2,55	2,55	2,56	2,56	2,56	2,57
C(3)-C(2)	1,38	1,38	1,38	1,39	1,39	1,39	1,39	1,40	1,40	1,40	1,40
C(4)-C(3)	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44
C(5)-C(4)	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,43	1,43	1,43
C(6)-C(5)	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39
C(7)-C(4)	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,44	1,43
C(8)-C(9)	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43
C(8)-C(6)	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43
C(9)-C(7)	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,40	1,40
F(10)-C(8)	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31
H(11)-C(2)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(12)-C(2)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(13)-C(3)	1,10	1,10	1,10	1,10	1,10	1,10	1,10	1,10	1,10	1,10	1,10
H(14)-C(7)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(15)-C(9)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(16)-C(6)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(17)-C(5)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09

Continuation of ***table 4***

Step number	12	13	14	15	16	17	18	19	20	21	22
C(2)-H(1)	2,40	2,40	2,40	2,30	2,30	2,30	2,30	2,30	2,30	2,30	2,30
C(3)-H(1)	2,10	2,00	1,90	1,80	1,70	1,60	1,50	1,40	1,30	1,20	1,10
C(2)-C(4)	2,57	2,57	2,57	2,57	2,56	2,55	2,54	2,53	2,52	2,51	1,59
C(3)-C(2)	1,41	1,41	1,41	1,42	1,42	1,43	1,44	1,45	1,46	1,48	1,50
C(4)-C(3)	1,45	1,45	1,46	1,47	1,47	1,48	1,49	1,50	1,50	1,51	1,60
C(5)-C(4)	1,43	1,43	1,42	1,42	1,42	1,42	1,42	1,42	1,42	1,42	1,47
C(6)-C(5)	1,40	1,40	1,40	1,40	1,40	1,40	1,40	1,40	1,40	1,40	1,38
C(7)-C(4)	1,43	1,43	1,43	1,42	1,42	1,42	1,42	1,42	1,42	1,42	1,47
C(8)-C(9)	1,43	1,43	1,43	1,42	1,42	1,42	1,42	1,42	1,42	1,42	1,44
C(8)-C(6)	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,43	1,44
C(9)-C(7)	1,40	1,40	1,40	1,40	1,40	1,40	1,40	1,40	1,40	1,40	1,38
F(10)-C(8)	1,31	1,31	1,32	1,32	1,32	1,32	1,32	1,32	1,32	1,32	1,30
H(11)-C(2)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,10
H(12)-C(2)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,10
H(13)-C(3)	1,10	1,10	1,10	1,10	1,10	1,11	1,11	1,11	1,12	1,13	1,10
H(14)-C(7)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(15)-C(9)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(16)-C(6)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(17)-C(5)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09

***Table 5**. Change in valence angles when the proton H_1 is attached to the β – carbon atom of p-fluoropyrene*

Step number	1	2	3	4	5	6	7	8	9	10	11
C(2)-C(3)-H(1)	77	73	72	72	71	71	74	74	77	81	80
C(3)-C(2)-H(1)	77	81	80	80	79	79	74	74	70	65	65
C(3)-C(2)-C(4)	26	26	26	26	26	26	26	26	26	26	26
C(4)-C(3)-C(2)	129	129	129	129	129	129	129	129	129	129	129
C(5)-C(4)-C(3)	124	124	124	124	124	124	124	124	124	124	124
C(6)-C(5)-C(4)	122	122	122	122	122	122	122	122	122	122	122
C(7)-C(4)-C(3)	119	119	119	119	119	119	119	119	119	119	119
C(8)-C(9)-C(7)	120	120	120	120	120	120	120	120	120	120	120
C(8)-C(6)-C(5)	120	120	120	120	120	120	120	120	120	120	120
C(9)-C(7)-C(4)	122	122	122	122	122	122	122	122	122	122	122
F(10)-C(8)-C(9)	120	120	120	120	120	120	120	120	120	120	120
H(11)-C(2)-C(4)	99	99	99	99	99	99	99	99	99	99	99
H(12)-C(2)-C(4)	147	147	147	147	147	147	147	146	146	146	146
H(13)-C(3)-C(2)	116	116	115	115	115	115	115	115	115	115	115
H(14)-C(7)-C(4)	120	120	120	120	120	120	120	120	120	120	120
H(15)-C(9)-C(7)	120	120	120	120	120	120	120	120	120	120	120
H(16)-C(6)-C(5)	120	120	120	120	120	120	120	120	120	120	120
H(17)-C(5)-C(4)	120	120	120	120	120	120	120	120	120	120	120

*Continuation of **table 5***

Step number	12	13	14	15	16	17	18	19	20	21	22
C(2)-C(3)-H(1)	84	88	92	90	94	99	103	108	113	118	124
C(3)-C(2)-H(1)	60	56	52	51	47	43	39	35	31	27	23
C(3)-C(2)-C(4)	26	27	27	27	28	29	30	31	32	33	62
C(4)-C(3)-C(2)	128	128	127	126	124	122	120	118	117	115	62
C(5)-C(4)-C(3)	124	124	123	123	123	122	122	121	121	120	118
C(6)-C(5)-C(4)	122	122	122	122	122	122	121	121	121	121	123
C(7)-C(4)-C(3)	119	119	119	119	119	120	120	120	120	121	118
C(8)-C(9)-C(7)	120	120	120	120	120	120	120	120	120	120	120
C(8)-C(6)-C(5)	120	120	120	120	120	120	120	120	119	120	120
C(9)-C(7)-C(4)	122	122	122	122	122	121	121	121	121	121	123
F(10)-C(8)-C(9)	120	120	120	120	120	120	120	120	120	120	120
H(11)-C(2)-C(4)	98	98	97	97	96	95	94	92	91	91	117
H(12)-C(2)-C(4)	147	147	147	148	148	149	150	151	153	152	117
H(13)-C(3)-C(2)	115	115	115	115	115	114	113	112	109	103	119
H(14)-C(7)-C(4)	120	120	120	120	120	120	120	120	120	120	119
H(15)-C(9)-C(7)	120	120	120	120	120	120	120	120	120	120	120
H(16)-C(6)-C(5)	120	120	120	120	120	120	120	120	120	120	120
H(17)-C(5)-C(4)	120	120	120	120	120	120	120	120	120	120	119

***Table 6**. Charge change when the proton H_1 is attached to the β – carbon atom of p-fluoropyrene*

Atom	1	2	3	4	5	6	7	8	9	10	11
H(1)	0,388	0,382	0,369	0,355	0,339	0,321	0,318	0,299	0,297	0,297	0,279
C(2)	0,059	0,047	0,048	0,048	0,049	0,050	0,071	0,075	0,101	0,130	0,140
C(3)	-0,011	0,006	0,016	0,028	0,041	0,055	0,044	0,059	0,047	0,034	0,046
C(4)	-0,102	-0,110	-0,119	-0,129	-0,140	-0,151	-0,154	-0,166	-0,169	-0,174	-0,186
C(5)	0,032	0,037	0,041	0,046	0,050	0,055	0,053	0,056	0,053	0,048	0,049
C(6)	-0,108	-0,110	-0,112	-0,113	-0,114	-0,116	-0,114	-0,115	-0,113	-0,110	-0,110
C(7)	0,048	0,052	0,056	0,060	0,065	0,069	0,067	0,071	0,068	0,065	0,067
C(8)	0,288	0,291	0,293	0,296	0,298	0,300	0,298	0,299	0,294	0,288	0,287
C(9)	-0,111	-0,113	-0,114	-0,116	-0,118	-0,119	-0,118	-0,119	-0,117	-0,115	-0,115
F(10)	-0,124	-0,124	-0,124	-0,124	-0,124	-0,124	-0,124	-0,124	-0,126	-0,128	-0,128
H(11)	0,075	0,075	0,077	0,079	0,081	0,083	0,085	0,087	0,089	0,092	0,094
H(12)	0,081	0,082	0,083	0,084	0,086	0,088	0,089	0,091	0,092	0,093	0,095
H(13)	0,082	0,082	0,083	0,084	0,084	0,085	0,086	0,087	0,088	0,089	0,091
H(14)	0,089	0,089	0,089	0,089	0,089	0,088	0,088	0,087	0,086	0,085	0,084
H(15)	0,117	0,117	0,117	0,117	0,118	0,118	0,118	0,118	0,117	0,116	0,116
H(16)	0,115	0,115	0,116	0,116	0,116	0,117	0,116	0,117	0,116	0,115	0,115
H(17)	0,081	0,081	0,080	0,080	0,080	0,080	0,079	0,079	0,077	0,075	0,074

*Continuation of **table 6***

Atom	12	13	14	15	16	17	18	19	20	21	22
H(1)	0,281	0,286	0,292	0,272	0,271	0,261	0,243	0,221	0,194	0,147	0,088
C(2)	0,177	0,217	0,261	0,284	0,334	0,384	0,430	0,470	0,498	0,512	0,074
C(3)	0,030	0,010	-0,014	-0,011	-0,040	-0,068	-0,090	-0,102	-0,102	-0,080	0,070
C(4)	-0,190	-0,195	-0,198	-0,203	-0,202	-0,201	-0,202	-0,205	-0,212	-0,215	-0,278
C(5)	0,042	0,032	0,019	0,015	0,003	-0,004	-0,006	-0,004	0,000	0,002	0,170
C(6)	-0,106	-0,101	-0,095	-0,092	-0,086	-0,082	-0,081	-0,081	-0,081	-0,082	-0,176
C(7)	0,062	0,056	0,050	0,049	0,041	0,033	0,027	0,020	0,015	0,014	0,171
C(8)	0,278	0,267	0,255	0,251	0,240	0,232	0,228	0,226	0,225	0,226	0,423
C(9)	-0,111	-0,106	-0,101	-0,098	-0,093	-0,088	-0,086	-0,084	-0,084	-0,084	-0,176
F(10)	-0,131	-0,134	-0,137	-0,138	-0,141	-0,143	-0,144	-0,145	-0,145	-0,144	-0,093
H(11)	0,097	0,100	0,103	0,106	0,108	0,110	0,111	0,112	0,114	0,115	0,084
H(12)	0,096	0,097	0,098	0,100	0,101	0,102	0,102	0,102	0,102	0,104	0,084
H(13)	0,094	0,097	0,102	0,105	0,110	0,114	0,118	0,121	0,128	0,135	0,080
H(14)	0,083	0,081	0,080	0,079	0,078	0,076	0,075	0,073	0,071	0,070	0,106
H(15)	0,115	0,114	0,112	0,112	0,110	0,109	0,109	0,108	0,108	0,108	0,134
H(16)	0,114	0,112	0,110	0,109	0,108	0,107	0,107	0,106	0,107	0,107	0,134
H(17)	0,070	0,067	0,063	0,061	0,058	0,058	0,059	0,061	0,063	0,066	0,106

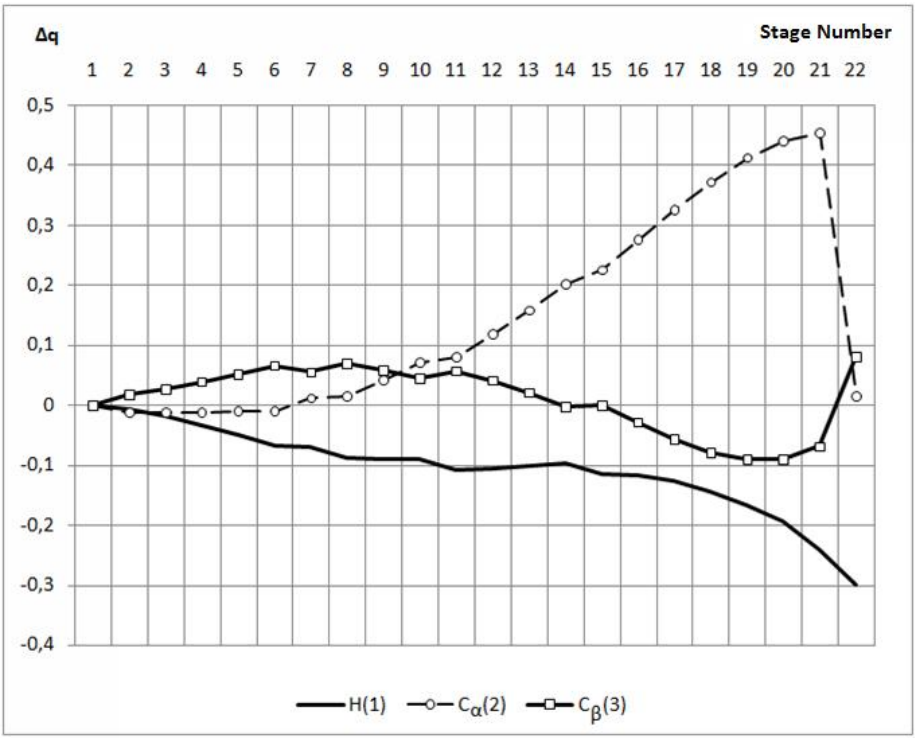

Fig. 8 - Change of charges on some atoms along the path of the addition of the proton H_1 to the β – carbon atom of p-fluorostyrene

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