INADEQUACY OF PI-APPROXIMATION IN HMO STUDY OF REACTIVITY OF FLUOROSUBSTITUTED BENZENOID HYDROCARBONS

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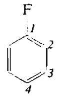
π- and σ-electronic structure of fluorobenzenes *I*–*XII* and perfluoronaphthalene (*XIII*) has been studied by means of the simple HMO and Del Re methods. The calculated electron charges are confronted with the reactivity of studied compounds towards ionic reagents and with fluorine chemical shifts in their NMR spectra. Correlations of HMO energies with electronic spectra and with ionization potentials are discussed.

Electronic effect of fluorine upon the reactivity of different positions of an aromatic system markedly differs from that of other halogens. For instance, electrophilic substitution of fluorobenzene (*I*) proceeds exclusively to the *para*-position, in contradistinction to other monohalobenzenes where the proportion of the *ortho*-substitution is much greater[1]. This order of reactivity has been succesfully interpreted within the framework of LCAO-MO method only by using a modified "interaction method" by L'Haya[2], not however by Pople's[3] version of SCF method. When using other reported π-electron densities, determined by various quantum chemical approaches (HMO[4], omega-technique[5], VESCF[6] and PPP[7]) and total electron densities (CNDO[8,9], PNDO[10]), we were unable to predict correctly the *para*-position as the most reactive in compound *I*. The above-mentioned data thus do not always correctly predict relative reactivities of different positions in the molecule.

In this work we attempted to estimate π- and σ-electronic structure of some fluorinated hydrocarbons by means of simple MO methods. In this connection it was of interest to find out whether by the use of a simpler parametrization better agreement between quantum chemical models and observed chemical and physical properties of the studied compounds can be achieved than with complicated parametrization used in theoretically more perfect procedures. With this aim we calculated π-electronic structure of fluorobenzenes *I*–*XII* and perfluoronaphthalene (*XIII*), using simple HMO method[11], and σ-electronic structure of these compounds, using Del Re method[12] based on isolated bicentric sigma-MO's.



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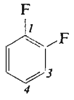

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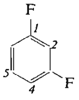

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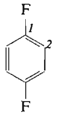

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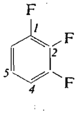

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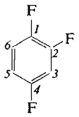

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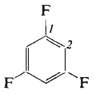

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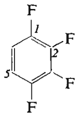

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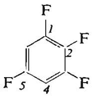
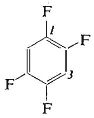
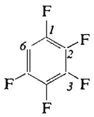


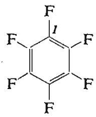
IX



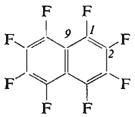
X



XI



XII



XIII

CALCULATIONS

HMO models of compounds *I*–*XIII* were calculated on a NE 803B digital computer, using program designed by V. Kvasnička (Computer Center of this Institute) and parametrization: h_F 3·0; k_{CF} 0·7 (*cf.*[13]). Sigma-electron charges were calculated by Del Re method, using the parametrization given in ref.[12].

RESULTS AND DISCUSSION

The HMO data obtained by us for compounds *I*–*XII* agree well with analogous literature data calculated with the use of identical[14] or somewhat modified[4,15–18] empirical parameters h_F and k_{CF}. On the other hand, the π-electron distribution obtained by us for most of the compounds greatly differs from that calculated by the interaction method[2]. It is of interest that bonding orbital energies for compounds *I*–*IV* are in several cases parallel to π-MO energies calculated by CNDO/2 method[8] (Fig. 1). This is especially true for bonding molecular orbitals localized on carbon atoms of the aromatic nucleus. On the other hand, HMO energies of molecular orbitals localized predominantly on fluorine atoms differ to much lesser extent, compared with the data obtained by CNDO/2 method.

Total electron charges, ξ^T which were calculated as the sum of Hückel π-charges, ξ^π, and Del Re σ-charges, ξ^σ, correlate well with analogous data calculated for compounds *I*–*IV*, *XI*, *XII* by CNDO/2 method[8,9] and for compounds *I*–*IV*, *VI*, *VII*, *X*–*XII* by PNDO method[10]. Correlation of this type is represented in Fig. 2, from which it is further seen that the data tend to split according to the type of atomic centers. This is most clearly demonstrated by the data for carbon atoms, for which the total electron charges obtained by CNDO/2 method are substantially more variable. It can be said that our values ξ^T are more comparable within individual groups according to positions. Notwithstanding, chemical behaviour of the studied compounds can be sucessfully predicted on the basis of these quantities, as will be shown later.

Chemical Reactivity

When comparing the reactivity indices calculated by HMO method for fluorobenzenes *I*–*XII* and perfluoronaphthalene (*XII*) (superdelocalizabilities for electrophilic and nucleophilic reactions, Wheland localization energies, the frontier and total π-electron densities, frontier orbital energies; *cf*[13]) with experimental reactivity we have found that these quantities do not correctly predict the reaction center. We assumed this could be due to the fact that in the calculations the effect of σ-system on the total reactivity of the fluoro derivatives *I*–*XIII* was not taken into account. The calculations of the σ-electronic structure supported this assumption in that the total charges (Table I), which include both the π- and σ-components, proved to be suitable qualitative criteria of the reactivity. Some of the results obtained are summarized in Table II.

Electrophilic protonation. The calculations are in agreement with the experimental data so far reported[19] for the fluoro derivatives *I*, *III*, *IV*, *VI*–*X*. The protonation takes place on the carbon atoms with the highest electron density, *i.e.* generally on fluorine-

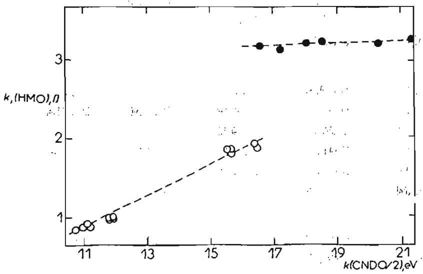


FIG. 1

Plot of Bonding MO Energies of Fluoro-Substituted Derivatives *I*–*XIII* against π-MO Energies Calculated[8] by CNDO/2 Method

● MO's localized predominantly of fluorine atoms; ○ MO's localized predominantly on the aromatic ring.

TABLE I

σ-, π- and Total Electron Charges in Compounds *I*—*XIII*

Compound	Position	C^a			F^a			H^a
		ζ^σ	ζ^π	ζ^T	ζ^σ	ζ^π	ζ^T	ζ^σ
I	1	0·2140	0·0316	0·2456	−0·2558	0·0271	−0·2287	—
	2	−0·0140	−0·0227	−0·0367	—	—	—	0·0325
	3	−0·0289	0·0012	−0·0277	—	—	—	0·0311
	4	−0·0304	−0·0158	−0·0462	—	—	—	0·0309
II	1	0·2303	0·0099	0·2402	−0·2533	0·0263	−0·2270	—
	3	−0·0123	−0·0218	−0·0341	—	—	—	0·0327
	4	−0·0285	−0·0145	−0·0430	—	—	—	0·0311
III	1	0·2159	0·0328	0·2487	−0·2555	0·0271	−0·2284	—
	2	0·0028	−0·0456	−0·0428	—	—	—	0·0341
	4	−0·0136	−0·0383	−0·0519	—	—	—	0·0326
	5	−0·0269	0·0025	−0·0244	—	—	—	0·0313
IV	1	0·2144	0·0163	0·2307	−0·2557	0·0264	−0·2293	—
	2	−0·0121	−0·0213	−0·0334	—	—	—	0·0327
V	1	0·2320	0·0107	0·2427	−0·2530	0·0263	−0·2267	—
	2	0·2465	−0·0122	0·2343	−0·2508	0·0255	−0·2253	—
	4	−0·0119	−0·0372	−0·0491	—	—	—	0·0327
	5	−0·0266	−0·0131	−0·0397	—	—	—	0·0313
VI	1	0·2307	−0·0054	0·2253	−0·2532	0·0256	−0·3376	—
	2	0·2322	0·0112	0·2434	−0·2530	0·0264	−0·2266	—
	3	0·0044	−0·0445	−0·0401	—	—	—	0·0343
	4	0·2166	0·0176	0·2342	−0·2555	0·0264	−0·2291	—
	5	−0·0116	−0·0370	−0·0486	—	—	—	0·0327
	6	−0·0104	−0·0204	−0·0308	—	—	—	0·0329
VII	1	0·2178	0·0339	0·2517	−0·2552	0·0272	−0·2280	—
	2	0·0032	−0·0611	−0·0579	—	—	—	0·0342
VIII	1	0·2324	−0·0043	0·2281	−0·2530	0·0256	−0·2274	—
	2	0·2482	−0·0111	0·2371	−0·2505	0·0255	−0·2250	—
	5	−0·0100	−0·0358	−0·0458	—	—	—	0·0329

TABLE I

(*Continued*)

Compound	Position	C[a]			F[a]			H[a]
		ξ^σ	ξ^π	ξ^T	ξ^σ	ξ^π	ξ^T	ξ^σ
IX	1	0·2339	0·0120	0·2459	−0·2527	0·0264	−0·2263	—
	2	0·2469	−0·0274	0·2195	−0·2507	0·0248	−0·2259	—
	4	0·0049	−0·0598	−0·0549	—	—	—	0·0343
	5	0·2182	0·0189	0·2371	−0·2551	0·0265	−0·2286	—
X	1	0·2326	−0·0040	0·2286	−0·2529	0·0257	−0·2272	—
	3	0·0062	−0·0433	−0·0371	—	—	—	0·0345
XI	1	0·2342	−0·0029	0·2313	−0·2526	0·0257	−0·2269	—
	2	0·2486	−0·0262	0·2224	−0·2504	0·0248	−0·2256	—
	3	0·2498	−0·0100	0·2398	−0·2502	0·0255	−0·2247	—
	6	0·0066	−0·0585	−0·0519	—	—	—	0·0345
XII	1	0·2502	−0·0249	0·2253	−0·2502	0·0249	−0·2253	—
XIII	1	0·2333	−0·0144	0·2189	−0·2528	0·0264	−0·2264	—
	2	0·2483	−0·0189	0·2294	−0·2505	0·0253	−0·2252	—
	9	0·0434	−0·0367	0·0067	—	—	—	—

[a] Atomic center.

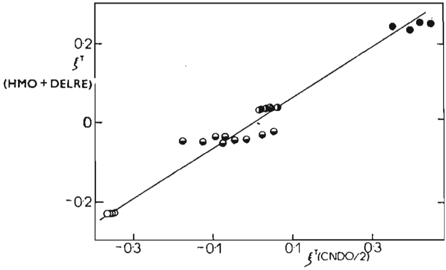


FIG. 2

Plot of Total Electron Charges Calculated by Combined HMO and Del Re Method against Electron Charges Calculated[8] by CNDO/2 Method

○ F; ◒ C(H); ◑ H; ● C(F).

TABLE II

Total Electron Densities ξ^T on Carbon Atoms of Compounds *I*–*XIII* and Experimental Reactivity

Compound	Order of densities[a]	Nucleophilic substitution		Electrophilic protonation	
		prediction[b]	experiment	prediction[b]	experiment[c]
I	$4 > 2 > 3 \gg 1$	$1 \gg 3$	—	$4 > 2 > 3$	4
II	$4 > 3 \gg 1$	$1 \gg 3$	—	$4 > 3$	—
III	$4 > 2 > 5 \gg 1$	$1 \gg 5$	—	$4 > 2 > 5$	4
IV	$2 \gg 1$	$1 \gg 2$	—	$2 \gg 1$	2
V	$4 > 5 \gg 2 > 1$	$1 > 2$	—	$4 > 5$	—
VI	$5 > 3 > 6 \gg 4 > 1 > 2$	$2 > 1 > 4$	—	$5 > 3 > 6$	5
VII	$2 \gg 1$	$1 \gg 2$	—	$2 \gg 1$	2
VIII	$5 \gg 1 > 2$	$2 > 1$	$2 > 1$[d]	$5 \gg 1$	—
IX	$4 \gg 2 > 5 > 1$	$1 > 5 > 2$	$1 > 2$[d]	$4 \gg 2$	4
X	$3 \gg 1$	$1 \gg 3$	—	$3 \gg 1$	—
XI	$6 \gg 2 > 1 > 3$	$3 > 1 > 2$	3[e] $> 1, 2$	$6 \gg 2$	—
XIII	$1 > 2$	$2 > 1$	$2 > 1$[f]	$1 > 2$	—

[a] The order derived from CNDO/2 data[8]: compound *I*: $2 > 4 > 3 \gg 1$; compound *II*: $3 > 4 \gg 1$; compound *III*: $2 > 4 > 5 \gg 1$; compound *IV*: $2 \gg 1$; [b] based on the magnitude of ξ^T; [c] ref.[19]; [d] ref.[21]; [e] ref.[22]; [f] ref.[26].

TABLE III

HMO Energy Data for Studied Compounds

HMO data are given in β-units.

Compound	W	k_2	k_1	k_{-1},	k_{-2},	$E(N \rightarrow V_1)$	$\tilde{\nu} . 10^{-3}$, cm^{-1}[a]	I, eV[b]
I	14·115	1·000	0·923	−1·000	−1·041	1·923	37·819	9·20
II	20·228	0·963	0·879	−1·021	−1·058	1·900	—	9·31
III	20·231	0·959	0·891	−1·020	−1·062	1·910	37·909	9·33
IV	20·230	1·000	0·852	−1·000	−1·081	1·852	36·843	9·15
V	26·340	0·891	0·874	−1·057	−1·062	1·931	—	—
VI	26·341	0·951	0·824	−1·026	−1·095	1·850	37·123	9·37
VII	26·347	0·891	0·891	−1·062	−1·062	1·953	38·527	9·3
VIII	32·450	0·877	0·816	−1·059	−1·100	1·875	—	9·61
IX	32·454	0·881	0·812	−1·062	−1·099	1·874	—	9·55
X	32·541	0·925	0·779	−1·042	−1·119	1·821	36·605	9·39
XI	38·561	0·849	0·779	−1·080	−1·119	1·860	—	9·84
XII	44·668	0·779	0·779	−1·119	−1·119	1·898	—	9·97
XIII	62·589	0·844	0·428	−0·749	−1·079	1·176	—	—

[a] Ref.[30]; [b] ref.[5].

unsubstituted carbon atoms. Fluorobenzene (*I*) is protonated in position 4, the protonation of 1,2,4-trifluorobenzene (*VI*) takes place in position 5. Benzonium ion, derived from 1,3,5-trifluorobenzene (*VII*), *i.e.* from the compound that has on its fluorine unsubstituted carbon atoms the electron density which is the highest of all the fluorobenzenes studied, is comparatively stable species. On the basis of experiments so far reported[19] it cannot be unambiguously decided whether the 3 or 2 position is first protonated in 1,3-difluorobenzene (*III*). The 3 position is preferred by our calculations.

Electrophilic nitration. Experiments[20] showed that pentafluorobenzene (*XI*) is about 10^2-10^3 less reactive than tetrafluorobenzenes *VIII* and *IX*. 1,2,4,5-Tetrafluorobenzene (*X*) did not react under similar experimental conditions, when nitrated by more efficient nitrating agent, it turned out to be less reactive than the pentafluoro derivative *XI*. Experimental order of the reactivity is therefore $X < XI < VIII, IX$. The following order of the reactivity can be predicted on the basis of the magnitude of the total charges ξ^T on fluorine-unsubstituted carbon atoms (Table I) $X < VIII < < IX$. Low yields of nitration prevented[20] to differentiate the reactivity of the isomers *VIII* and *IX*. The location of pentafluorobenzene (*XI*) is of interest. According to the

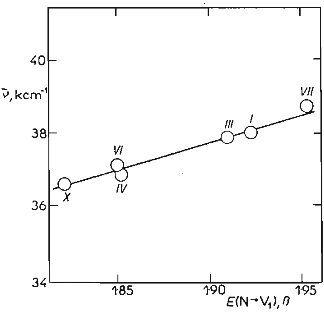


FIG. 3

Wavenumbers of Longest Wavelenght Absorption Bands in UV Spectra of Fluoro Derivatives *I*, *III*, *IV*, *VI*, *VII*, and *X* against Energies $E(N \rightarrow V_1)$ Calculated by HMO Method

The wavenumbers taken from ref.[30] and the references cited therein.

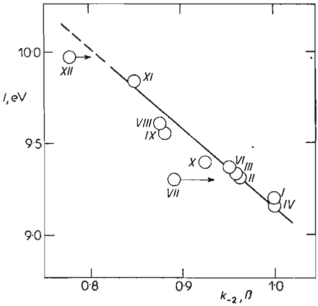
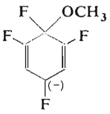


FIG. 4

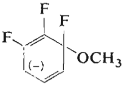
Dependence of Ionization Potentials of Fluoro Derivatives *I*—*IV*, *VI*—*XII* on Energies of Second Highest MO Calculated by HMO Method

The ionization potentials taken from ref.[5] and the references cited therein.

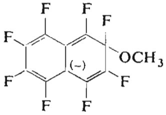
magnitude of the total changes ξ^T it should be placed between the compounds *VIII* and *IX*. This compound has however only one reaction center, which is likely the reason of its lower reactivity.



IXa



IXb



XIIIa

Nucleophilic substitution. It follows from experimental data on nucleophilic substitution of fluorine in polyfluorinated aromatic hydrocarbons[21,22] that the exchange of fluorine proceeds most slowly when other fluorine atom is attached to the *para*-position to the reaction center. This is thought[21] to be due to differences between energies of transition states *IXa* and *IXb*, which are caused by repulsive effect of fluorine atom in the *para*-position to the negative charge, *i.e.* by the so-called "I-repulsion"[22-25]. The orientation of nucleophilic substitution in perfluoronaphthalene to the 2 position (the intermediate *XIIIa*) has been explained similarly[26]. The values of Wheland localization energies, which can be considered as π-approximation of the mentioned energy differences (in compound *IX* $2\cdot761\beta$ for position 2 and $2\cdot655\beta$ for position 4; in compound *XIII* $2\cdot530\beta$ for position 1 and $2\cdot693\beta$ for position 2) cannot be reconciled with the above explanation. On the other hand, the experimental

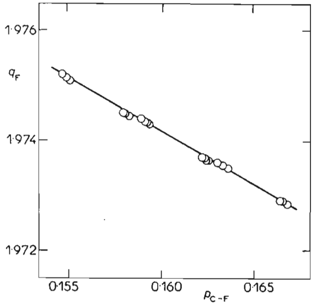


FIG. 5

C—F Bond Orders against π-Electron Densities on Fluoride in HMO Models of Compounds *I*–*XII* reactivity is correctly predicted by the magnitude of the total charges ξ^T on fluorine-substituted carbon atoms, where nucleophilic substitution always occurs in the positions with lower electron density, *e.g.* in 1,2,3,4-tetrafluorobenzene (*VIII*) in the 2 position and in 1,2,3,5-tetrafluorobenzene (*IX*) in the 1 position. In 1,2,4,5-tetrafluorobenzene (*X*), where fluorine-substituted carbon atoms are electron-richest (relative to the analogous carbon atoms in the derivatives *VIII* and *IX*) and where each fluorine atom is in the *para*-position to another fluorine atom, nucleophilic substitution proceeds most slowly[21]. Experimental order of the reactivity *IX* > > *VIII* > *X* parallels the order of values of ξ^T. Nucleophilic substitution in pentafluorobenzene (*XI*) occurs in position 3, which is, according to the calculation, the site of lowest electron density. Similar agreement between the experimental reactivity and the calculation has also been observed for perfluoronaphthalene (*XIII*) where position 2 is predicted to be the most reactive.

Nucleophilic hydrogen isotopic exchange. The exchange of deuterium and tritium in fluorobenzene (*I*) catalyzed by lithium cyclohexylamide proceeds *via* the rate-determining step that involves the cleavage of the carbon–deuterium[27] (tritium) bond the deuterium atom of which becomes the reaction center (Scheme 1). Studies on hydrogen isotopic exchange in aliphatic halogeno derivatives, *e.g.* on deuterium exchange in haloforms, showed[28] that σ-electron density on hydrogen atoms becomes criterion of the reactivity, since the structure of the activated complex is similar

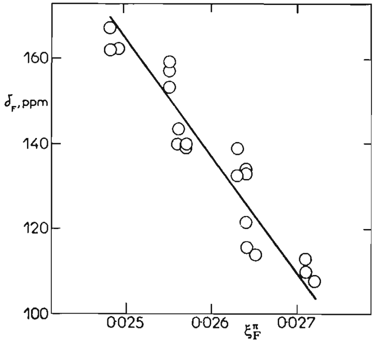
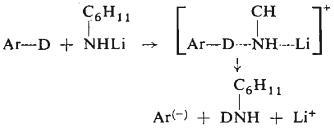


Fig. 6

F-NMR Chemical Shifts in Compounds *I*—*XII* against π-Charges on Fluorine Calculated by HMO Method

The chemical shifts taken from ref.[10] and the references cited therein. The data below the line correspond to fluorine atoms in mutual *para*-position.

to that of the reactants. Isotopic exchange of deuterium and tritium in compound *I* proceeds[27] in the following order of positions 2 > 3 > 4, which parallels the change in the magnitude of the total charges ξ^T on hydrogen atoms (Table I). Isotopic exchange of tritium and deuterium in polyfluorobenzenes[29] *VIII*–*XI* in methanolic methylate also proceeds *via* the primary cleavage of the carbon–tritium (deuterium) bond, but without primary isotope effect ("internal return type"[29]). The experimental order of the reactivity of tetrafluorobenzenes[29] *X* > *IX* > *VIII* is correctly predicted both by the σ-electron charges ξ^σ on hydrogen atoms and by the σ-electron charges on fluorine-unsubstituted carbon atoms (Table I).



$$\mathrm{Ar{-}D} + \underset{}{\overset{\mathrm{C_6H_{11}}}{\mathrm{NHLi}}} \rightarrow \left[\mathrm{Ar{-}D \cdots \overset{\mathrm{CH}}{N}H \cdots Li}\right]^+ \rightarrow \mathrm{Ar^{(-)}} + \overset{\mathrm{C_6H_{11}}}{\mathrm{DNH}} + \mathrm{Li^+}$$

Scheme 1

Physical Properties

Electronic absorption spectra. We compared the, calculated energies $E(\mathrm{N} \rightarrow \mathrm{V_1})$ of the one-electron transition between frontier molecular orbitals (see Table III)

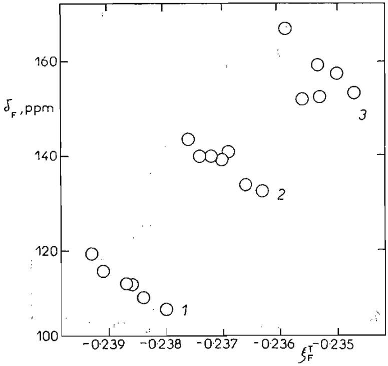


FIG. 7

F-NMR Chemical Shifts in Compounds *I*–*XII* against Total Charges on Fluorine Atoms

The chemical shifts taken from ref.[10] and the references cited therein. *1* No *ortho*-interaction with fluorine atoms, *2* one *ortho*-interaction, *3* two *ortho*-interactions.

with the observed wavenumbers of the longest wavelength absorption bands in the UV spectra of compounds *I*, *III*, *IV*, *VI*, *VII*, and *X* (see ref.[30] and references cited therein). It is seen from Fig. 3 that there exist a linear correlation between these two quantities, which upon treatment by the least square method has the form

$$\tilde{\nu} \,.\, 10^{-3}\,(\mathrm{cm}^{-1}) = 14{\cdot}66\, E(\mathrm{N} \rightarrow \mathrm{V}_1)\,(\beta) + 9{\cdot}85\,; \quad r = 0{\cdot}9806 \quad \text{(for 6 couples)}.$$

This circumstance could be attributed to the constant and significant weight of the $\mathrm{N} \rightarrow \mathrm{V}_1$ transition upon excitation, which corresponds to the long-wavelength absorption band. Unfortunately, in the earlier studies[3,7], where the LCI method was used, these data have not been reported.

Ionization potentials. We have not found any statistically significant correlation between the first ionization potentials of the compounds *I*–*IV*, and *VI*–*XII* and the HOMO energies calculated by the HMO method. This is in harmony with the earlier results of Caldow and Coulson, who for the same series of the compounds proved the invalidity of Koopman theorem[5] by a modified omega-technique. Statistically significant correlation between the first ionization potential and the energy k_2 (Fig. 4) is fortuitous:

$$I\,(\mathrm{eV}) = -4{\cdot}11 k_2\,(\beta) + 13{\cdot}22\,; \quad r = 0{\cdot}9321 \quad \text{(for 11 couples)}\,.$$

NMR *Spectra.* In this field our attention centered on the verification of theoretical conclusions made by Karplus and Das[16], and by Prosser and Goodman[31]. These authors pointed out that fluorine chemical shift in aromatic compounds depends mainly on the π-electron density on fluorine, q_{F}, and on the bond order of the corresponding π-bond, p_{CF}. As within the framework of the HMO approximation these quantities are linearly dependent (Fig. 5), we first attempted to correlate π-charges $\xi_{\mathrm{F}}^{\pi} = 2 - q_{\mathrm{F}}$ with chemical shifts δ_{F} (see[10] and references cited therein). In order to check the correctness of our assumption, we correlated also δ_{F} with the total charges $\xi_{\mathrm{F}}^{\mathrm{T}}$. It is evident from Figs 6 and 7 that better correlation is obtained with the π-electron charges, as expected, the relation being

$$\delta_{\mathrm{F}} = -27731{\cdot}6\xi_{\mathrm{F}}^{\pi} + 857{\cdot}7\,; \quad r = 0{\cdot}9387 \quad \text{(for 20 couples)}\,.$$

This finding is in harmony with the above-mentioned theory[16,31]. When the total charges $\xi_{\mathrm{F}}^{\mathrm{T}}$ were in the correlation, the correlation field split into three groups according to the number of the *ortho*-interactions with fluorine atoms in the individual derivatives (Fig. 7).

CONCLUSION

Quantum chemical description of the electronic structure of the fluoro-substituted benzenoid hydrocarbons *I–XIII* based on combination of the π-electron HMO approximation with the σ-electron approximation of Del Re appears to be quite necessary for description of the behaviour of these compounds in heterolytic reactions. The predictions based on the so obtained total electron charges on individual atomic centers are equivalent to or even better than those based on the charges calculated by more perfect CNDO/2 and PNDO methods. On the other hand, some physical properties can be successfully correlated even with HMO π-electron data.

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