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Quantum-Chemical Interpretation of the Effect of Substitution in the Benzene Ring on the Reactivity of Monosubstituted Benzenes

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Abstract—The HF/3-21G and HF/6-31G** methods were used to calculate the effective charges on the carbon and hydrogen atoms in the *meta* and *para* positions of the aromatic ring in monosubstituted benzenes. The calculated charges are compared with the Hammett constants of the substituents in the aromatic ring. Linear correlations were obtained between the atomic charges and the Hammett constants of the substituents. The resulting equations were shown to be useful for predicting and assessing the reactivity of aromatic compounds.

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Investigations into organic structure–reactivity relationships relate to actual problems of contemporary organic chemistry. With aromatic compounds, substituent σ constants are often used. Recently these parameters were complemented by various quantum-chemical descriptions, such as atomic charges that characterize such a fundamental property of atoms as electronegativity [1], as well as electrostatic potential, ionization potential, distribution of π-electron density, etc. [2–5].

Earlier we showed [6] that the reactivity of substituted nitrobenzenes can be assessed in terms of charges on the nitro groups, which correlate with the σ constants of the corresponding substituents. We considered it interesting to extend this approach to various monosubstituted aromatic compounds and to compare the descriptors of electronic structure (effective charges on the carbon and hydrogen atoms of the benzene ring) obtained by ab initio calculations with the classical Hammett constants of various substituents with the aim to find out whether such descriptors are feasible for reactivity assessment of aromatic compounds.

The quantum-chemical calculations of substituted benzenes were carried out by the ab initio HF/3-21G and HF/6-31G** methods with full geometry optimization and control of the type of stationary points on the potential energy surface (PES). The latter was performed by calculating the spectra of normal-mode vibrations for each stationary point: The lack of negative-frequency bands in the calculated spectrum was considered evidence showing that a minimum on the PES is attained.

We calculated effective charges on the carbon and hydrogen atoms in the *meta* and *para* positions of the aromatic ring for a series of monosubstituted aromatic compounds Ph–X, where X = H, Me, Et, Pr, *i*-Pr, *t*-Bu, OH, OMe, OEt, SH, SMe, $Si(Me)_3$, NH_2, NHMe, NHEt, $N(Me)_2$, NHOH, $NHNH_2$, NHAc, F, Cl, COOH, COOMe, COOEt, $CONH_2$, CHO, Ac, $COCF_3$, CN, SO_2Me, SO_2NH_2, SO_2CF_3, CF_3, NO_2, N^+H_3, N^+H_2Me, $N^+(Me)_3$, $S^+(Me)_2$, COO^-, SO_3^-, and O^-. The choice of substrates for the calculations was motivated by the availability in reference literature of the corresponding substituent σ constants [7].

The calculated effective charges on the carbon and hydrogen atoms in the *meta* and *para* positions of the aromatic ring in monosubstituted benzenes are compared with substituent σ constants. We found that the charges on the *meta*-carbon atoms of the benzene ring do not correlate directly with the σ constants of the substituents, but the effective charges on *meta*- and *para*-hydrogen atoms do correlate with the σ constants The $q(H) = f(\sigma)$ dependences for the *meta* and *para*

positions and the $q(C)^{para} = f(\sigma)$ dependence are described by linear equations with fairly high correlation coefficients. The $q(H) = f(\sigma)$ dependence for the *meta* and *para* positions splits into two: one for neutral substituents and the other for ionic substituents.

Equations for neutral substituents (HF/3-21G charges).

$$q(H)^{meta} = (0.239 \pm 0.001) + (0.032 \pm 0.001)\sigma^{meta}, \quad r\ 0.95, \quad (1)$$

$$q(H)^{para} = (0.243 \pm 0.001) + (0.022 \pm 0.001)\sigma^{para}, \quad r\ 0.96, \quad (2)$$

$$q(C)^{para} = (-0.245 \pm 0.001) + (0.042 \pm 0.002)\sigma^{para}, \quad r\ 0.95. \quad (3)$$

Equations for ionic substituents (HF/3-21G charges).

$$q(H)^{meta} = (0.213 \pm 0.004) + (0.083 \pm 0.004)\sigma^{meta},\ r\ 0.99, \quad (4)$$

$$q(H)^{para} = (0.202 \pm 0.013) + (0.078 \pm 0.015)\sigma^{para},\ r\ 0.93. \quad (5)$$

Equations for neutral substituents (HF/6-31G** charges).

$$q(H)^{meta} = (0.149 \pm 0.004) + (0.028 \pm 0.001)\sigma^{meta},\ r\ 0.97, \quad (6)$$

$$q(H)^{para} = (0.151 \pm 0.001) + (0.019 \pm 0.001)\sigma^{para},\ r\ 0.95. \quad (7)$$

$$q(C)^{para} = (-0.154 \pm 0.001) + (0.044 \pm 0.004)\sigma^{para},\ r\ 0.93. \quad (8)$$

Equations for ionic substituents (HF/3-21G charges).

$$q(H)^{meta} = (0.119 \pm 0.004) + (0.084 \pm 0.005)\sigma^{meta},\ r\ 0.99. \quad (9)$$

$$q(H)^{para} = (0.105 \pm 0.013) + (0.074 \pm 0.014)\sigma^{para},\ r\ 0.95. \quad (10)$$

Comparing Eqs. (4) and (5) and (9) and (10) one can see that, irrespective of whether the ionic substituent is in the *meta* or *para* position, the atomic charge on hydrogen is described by the same equation. In whole, the σ constants of ionic substituents are more sensitive to the atomic charge on hydrogen that the σ constants of neutral substituents.

According to the calculation results, the positive charge on the *meta*- and *para*-hydrogen atoms of the aromatic ring is increased, compared to that in the unsubstituted benzene, by substituents that exert a *–I* effect and decreased by substituents that exert a *+I* effect, which is consistent with classical views. Conjugation cannot affect the charge on hydrogen atoms, since the electrons of the latter are not involved in the π-electron system of the benzene ring.

By reverse calculation by Eqs. (1), (2) and (4), (5) we obtained the Hammett constants σ_{calc} (see Table). They are nicely consistent with experimental values and form with them dependences with a free term tending to zero and a slope close to 1.

Effective charges on the hydrogen atoms in the *meta* and *para* positions of the benzene ring in monosubstituted benzenes $q(H)$, calculated by Eqs. (1), (2) and (4), (5), and published Hammett constants σ_{calc} and σ_{exp} [7]

X	$q(H)^{meta}$ a	$q(H)^{meta}$ b	σ_{exp}^{meta}	σ_{calc}^{meta}	$q(H)^{para}$ a	$q(H)^{para}$ b	σ_{exp}^{para}	σ_{calc}^{para}
H	0.239	0.148	0	0.023	0.239	0.148	0	–0.182
Me	0.238	0.147	–0.069	–0.031	0.237	0.146	–0.17	–0.273
Et	0.237	0.146	–0.07	–0.07	0.236	0.145	–0.151	–0.318
Pr	0.236	0.145	–0.05	–0.094	0.236	0.145	–0.151	–0.318
i-Pr	0.236	0.146	–0.1	–0.094	0.237	0.146	–0.197	–0.273
t-Bu	0.236	0.146	–0.1	–0.094	0.236	0.146	–0.197	–0.318
OH	0.244	0.151	0.121	0.156	0.239	0.147	–0.37	–0.182
OMe	0.242	0.149	0.115	0.094	0.237	0.145	–0.268	–0.273
OEt	0.241	0.148	0.1	0.063	0.237	0.145	–0.24	–0.273
SH	0.247	0.154	0.25	0.25	0.245	0.152	0.15	0.091
SMe	0.243	0.153	0.15	0.125	0.243	0.150	0	0
$Si(Me)_3$	0.237	0.146	–0.04	–0.063	0.240	0.148	–0.07	–0.136
NH_2	0.236	0.144	–0.16	–0.094	0.229	0.139	–0.66	–0.636
NHMe	0.235	0.145	–0.3	–0.125	0.229	0.141	–0.84	–0.636
NHEt	0.235	0.144	–0.24	–0.125	0.228	0.140	–0.61	–0.681

Table (Contd.)

X	$q(H)^{meta\ a}$	$q(H)^{meta\ b}$	σ_{exp}^{meta}	σ_{calc}^{meta}	$q(H)^{para\ a}$	$q(H)^{para\ b}$	σ_{exp}^{para}	σ_{calc}^{para}
$N(Me)_2$	0.234	–	–0.05	–0.156	0.229	–	–0.83	–0.636
NHOH	0.241	0.148	–0.04	0.063	0.237	0.145	–0.34	–0.273
$NHNH_2$	0.233	0.144	–0.02	–0.188	0.227	0.140	–0.55	–0.727
NHAc	0.241	–	0.21	0.063	0.238	–	0	–0.227
F	0.253	0.159	0.337	0.438	0.247	0.154	0.062	0.182
Cl	0.255	0.160	0.373	0.5	0.252	0.157	0.227	0.409
COOH	0.249	0.158	0.37	0.313	0.251	0.159	0.45	0.364
COOMe	0.248	–	0.32	0.281	0.249	–	0.39	0.273
COOEt	0.247	–	0.37	0.25	0.248	–	0.45	0.227
$CONH_2$	0.248	0.158	0.28	0.281	0.249	0.157	0.36	0.273
CHO	0.250	0.159	0.36	0.344	0.251	0.160	0.22	0.364
Ac	0.245	0.158	0.376	0.188	0.249	0.157	0.502	0.273
$COCF_3$	0.257	0.164	0.65	0.563	–	–	–	–
CN	0.256	0.167	0.56	0.531	0.256	0.166	0.66	0.591
SO_2Me	0.261	–	0.56	0.688	0.260	–	0.68	0.773
SO_2NH_2	0.260	–	0.55	0.656	0.260	–	0.62	0.773
SO_2CF_3	0.269	–	0.79	0.938	0.268	–	0.93	1.136
CF_3	0.255	0.161	0.43	0.5	–	–	–	–
NO_2	0.263	0.171	0.71	0.75	0.263	0.170	0.778	0.909
N^+H_3	0.302	0.211	1.13	1.072	0.303	0.210	1.70	1.295
N^+H_2Me	0.298	0.207	0.96	1.024	–	–	–	–
$N^+(Me)_3$	0.292	–	0.88	0.952	0.294	–	0.82	1.179
$S^+(Me)_2$	0.294	0.204	1	0.976	0.299	0.208	0.9	1.244
COO^-	0.193	0.102	–0.1	–0.241	0.191	0.099	0	–0.141
SO_3^-	0.214	0.116	0.05	0.012	0.210	0.112	0.09	0.103
O^-	0.162	0.068	–0.71	–0.614	0.148	0.058	–0.52	–0.692

[a] 3-21G charges. [b] 6-31G** charges.

Equations for neutral substituents.

$$\sigma_{calc}^{meta} = (0.027 \pm 0.021) + (0.90 \pm 0.06)\sigma_{exp}^{meta},\ r\ 0.94, \quad (11)$$

$$\sigma_{calc}^{para} = (0.018 \pm 0.024) + (0.92 \pm 0.05)\sigma_{exp,}^{para}\ r\ 0.96. \quad (12)$$

Equations for ionic substituents.

$$\sigma_{calc}^{meta} = (0.010 \pm 0.043) + (0.98 \pm 0.05)\sigma_{exp}^{meta},\ r\ 0.99, \quad (13)$$

$$\sigma_{calc}^{para} = (0.064 \pm 0.153) + (0.87 \pm 0.17)\sigma_{exp}^{para},\ r\ 0.93. \quad (14)$$

Since Eqs. (11)–(14) have close parameters, we can use instead of them a single common equation (15).

$$\sigma_{calc} = (0.024 \pm 0.016) + (0.92 \pm 0.03)\sigma_{exp},\ r\ 0.96. \quad (15)$$

Thus, the descriptors of electronic structure, such as the effective charges on the hydrogen atoms in the *meta* and *para* positions of the benzene ring, obtained by ab initio calculations, and the equations obtained on their basis can be used to predict the reactivity of monosubstituted benzenes containing substituents whose experimental Hammett constants are unavailable.

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