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Journal of Fluorine Chemistry 128 (2007) 857–861

JOURNAL OF FLUORINE CHEMISTRY

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A qualitative scale for the electron withdrawing effect of substituted phenyl groups and heterocycles

Berthold Hoge *, Julia Bader

Institut für Anorganische Chemie, Universität zu Köln, D-50939 Köln, Germany

Received 27 February 2007; received in revised form 2 April 2007; accepted 4 April 2007
Available online 8 April 2007

Abstract

The electron withdrawing effect of a variety of differently substituted phenyl groups can be classified on the basis of the C–O or C–N distance of the corresponding phenolate or aryl amide ions (Ar–O^- and Ar–NH^-), respectively, which are reliably accessible by DFT calculations on B3LYP/6-311 + G(2d,p) level of theory. An increasing electron withdrawing effect of the aromatic group leads to a shortened C–O and C–N distance of the corresponding ions. Within the presented model it is also possible to characterize the electronic nature of different kinds of six membered heterocycles.

The defined constants $\Delta(E)_{m,p}$ – the difference of the E–C distances of the substituted derivatives X-C_6H_4-E and the non-substituted phenyl derivative, C_6H_5-E – exhibit the same tendency as the corresponding Hammett constants. The values of $\Delta(E)_{m,p}$ strongly depend on the nature of E. With E = F, the resulting values $\Delta(F)_{m,p}$ are found to be accidentally close to the corresponding Hammett constants. Therefore, the values of $\Delta(E)_{m,p}$, which can be easily determined by DFT calculations, are useful tools to classify the electronic nature of different kinds of substituents.

The different electronic nature of the groups E, for example O^-, NH^- or F, gives rise to varying electronic interactions with the connected aromatic ring system. These interactions influence on their part the special interaction of a given substituent X. This is the reason why the constants $\Delta(E)_{m,p}$ exhibits different values, which vary depending on the different electronic nature of the groups E. As a consequence, the values $\Delta(E)_{m,p}$ open the possibility to classify the electronic nature of substituents X in relation to any neutral or even charged group E.

Keywords: Hammett; DFT; Electron-withdrawing groups; Triazin; Perfluoroorganyl

1. Introduction

The Hammett equation as introduced in the 1930s [1] and its extended forms [2] have been established as the most general and simplest approach to describe structure-property relations. Although the Hammett methodology has been criticized by theoreticians due to its empirical basis, it is noteworthy that σ constants, easily obtained from the ionization of organic acids in solution, can often be used to successfully predict equilibria and rate constants for a variety of chemical reactions [2].

The values of σ were defined by Hammett from the ionization constants of benzoic acids as follows:

$$\sigma_{m,p}\,\rho = \log K_X - \log K_H \qquad (1)$$

where K_H is the ionization constant for benzoic acid in water at 25 °C and K_X is the corresponding constant for a *meta*- or *para*-substituted benzoic acid, X-C_6H_4-CO_2H. The proportionality constant ρ characterizes the given reaction and is set at 1.00 for ionization of X-C_6H_4-CO_2H in water at 25 °C. The values of the Hammett constants σ_m and σ_p summarize the total electronic effects, consisting of resonance and field inductive effects, of a group X bound to a benzene ring. A positive value of σ indicates an electron-withdrawing group; a negative value an electron-donating group. Due to sterical factors, this method usually fails for substituents in *ortho* position. The Hammett equation has been shown to be applicable to physical measurements, including vibrational frequencies and NMR spectroscopic chemical shifts.

To determine the σ constants of functional groups by quantum chemical methods, the Hammett equation is best expressed in energy terms:

$$\sigma_{m,p}\,\rho = E_X - E_H \qquad (2)$$

Usually, the symbols E_X and E_H for the substituted and unsubstituted derivatives are expressed as Gibbs energy or activation Gibbs energy [3].

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* Corresponding author. Tel.: +49 221 470 3911; fax: +49 221 470 5196.
E-mail address: b.hoge@uni-koeln.de (B. Hoge).

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doi:10.1016/j.jfluchem.2007.04.007

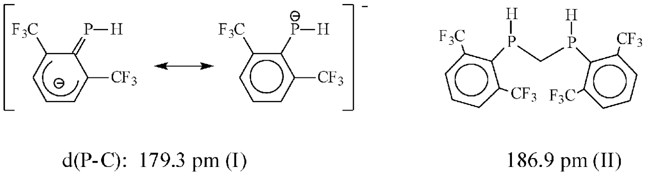
The classification of the electronic effects σ of a given group X by quantum chemical calculations using Eq. (2) is a complex and time-consuming process. As to be expected, the calculated data are not directly comparable with the corresponding experimental values.

The influence of electron-withdrawing groups in phosphorus chemistry is essential for example for the realization of (i) organic *n*-type semiconductors [4], (ii) chiral π-acidic phosphane ligands [5] as well as for the stabilization of (iii) phosphinous acids [6] and (iv) low valent phosphorus species [7,8]. The tabulated Hammett constants σ are useful values to guide the synthetic work in these areas but the determination of values for so far not listed groups by quantum chemical calculation is not feasible.

The subject of this paper is an empirical approach to determine the relative electronic effect of different kinds of substituents X by DFT calculations.

2. Results and discussion

Bertrand and coworkers presented the synthesis and single crystal structure analysis of $[K([15]crown\text{-}5)_2][2,6\text{-}(CF_3)_2C_6H_3PH]$ [9]. The aryl phosphanide ion (I) exhibits a surprisingly short P–C distance of 179.3(6) pm, which is more than 7 pm shorter in comparison with the corresponding neutral diphosphanylmethane derivative (II).



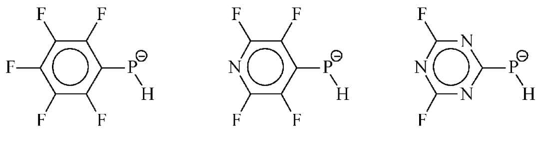
d(P-C): 179.3 pm (I) 186.9 pm (II)

(3)

This shortening can be attributed to additional resonance structures and to the strong electron withdrawing effect of the 2,6-bis(trifluoromethyl)phenyl group. The experimental C–P distance of 179.3(6) pm is in good agreement with the theoretical value of 178.7 pm obtained at the B3LYP/6-31 + G(d,p) level of theory [10].

Based on these observations, the question arises whether the P–C distances of aryl phosphanide ions with different substituents bound to the aryl groups can be used to classify the electronic effects of aromatic ring systems. One advantage of this method is the fact that reliable values of the C–P distances are easily accessible by DFT calculations.

In a preliminary paper [11], we presented the calculated C–P distances of $C_6F_5PH^-$ (III), *p*-$C_5NF_4PH^-$ (IV) and *s*-$C_3N_3F_2$-PH^- (V), which were calculated to 180.2, 177.8 and 174.7 pm, respectively, at the B3PW91/6-311G(d,p) level of theory.



d(C-P): 180.2 pm (III) 177.8 pm (IV) 174.7 pm (V)

(4)

The order of P–C bond lengths from 180.2 pm (III) via 177.8 pm (IV) to 174.7 pm (V) implies an increasing electron withdrawing effect on replacing successively CF groups by isolobal nitrogen atoms.

The increased electron withdrawing effect of the *p*-tetrafluoropyridyl group compared to that of a pentafluorophenyl group has already been established by the increased stabilization of the unusual phosphinous acid $R_2P\text{-}O\text{-}H$ with respect to the phosphane oxide tautomer $R_2P(O)H$ [6]. Furthermore, bis(*p*-tetrafluoropyridyl)phosphane ligands have shown to be stronger π-acidic ligands in transition metal complexes than their corresponding bis(pentafluorophenyl)-phosphane derivatives [5].

These results indicate that the calculated C–P distances of aryl phosphanide ions can in principle be used to classify the electron withdrawing effect of the corresponding aryl groups.

Due to the in some extend inaccurate description of third row elements by quantum chemical calculations, it is more feasible to replace the phosphorus atom by a nitrogen atom, leading to aryl amide ions, $Ar\text{–}N(H)^-$. To investigate the steric and electronic effects of the hydrogen atom which is located in the plane of the aromatic substituent it is necessary to compare the C–N distances of aryl amide ions with the corresponding C–O distances of the isolobal phenolate ions, $Ar\text{–}O^-$.

Fig. 1 depicts a plot of the calculated [12] C–N distances of different aryl amide derivatives versus the C–O distance of the corresponding phenolate ions. The polynomial trend line, $d(\text{C–N}) = 0.04\ d^2(\text{C–O}) - 8.75\ d(\text{C–O}) + 613$, proves that the electronic characteristics of different aromatic groups can be described by either the C–N distances of the corresponding aryl amide ions or by the C–O distances of the corresponding phenolate ions. Surprisingly, even the electronic characteristics of aromatic groups with one or two steric demanding trifluoromethyl groups in *ortho* position to the oxide or amide function are equally described (data points nos. 20, 21 and 23 in Fig. 1; the numbering scheme of the data points is borrowed from the serial number of Table 1).

The data points for 2-pyridine derivatives (data points 19_{cis} and 19_{trans}) exhibit a significant deviation from the trend line in Fig. 1. For the two $2\text{-}C_5H_4N\text{–}N(H)^-$ conformers ($19\text{-}N_{cis}$) and ($19\text{-}N_{trans}$), significantly different C–N distances are calculated (comp. Eq. (3)). Therefore, it is probable that an interaction of

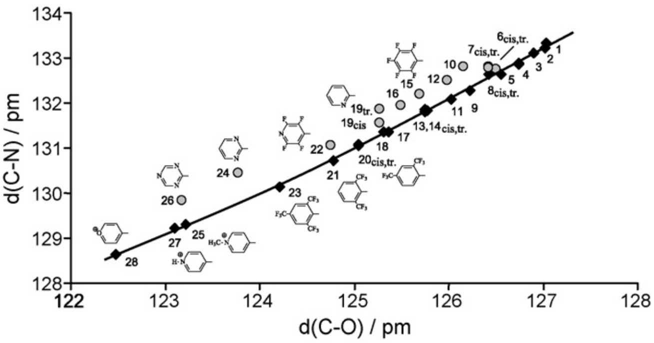


Fig. 1. C–N distances of different aryl amide derivatives vs. the C–O distance of the corresponding phenolate ions (the numbering schema of the data points is borrowed from the serial number of Table 1).

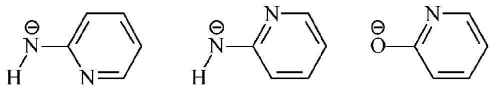
Table 1
Calculated[a] *d*(C–O) and *d*(C–N) distances (pm) of phenolate and aryl amide derivatives

No.	Aromatic substituent	*d*(C–O)	*d*(C–N)$_{cis/trans}$[b]
1	p-C_6H_4F	127.038	133.336
2	p-$C_6H_4CH_3$	127.017	133.232
3	C_6H_5	126.905	133.108
4	m-C_5H_4N	126.740	132.851/132.890
5	m,m-$C_3H_3N_2$	126.552	132.641
6	m-C_6H_4F	126.502	(132.742)/(132.740)
7	o-C_6H_4F	126.421	(132.795)/(132.764)
8	m-$C_6H_4CF_3$	126.418	132.634/132.640
9	p-C_5H_4N	126.219	132.272
10	s-$C_6H_3F_3$	126.161	(132.812)
11	p-$C_6H_4CF_3$	126.028	132.079
12	o,o-$C_6H_3F_2$	125.990	(132.508)
13	p-C_6H_4CN	125.779	131.836
14	o-$C_6H_4CF_3$	125.744	131.819/131.866
15	C_6F_5	125.692	(132.196)
16	p-C_6F_4H	125.497	(131.958)
17	p-C_6H_4-s-$C_3H_2N_3$	125.368	131.362
18	p-$C_6H_4NO_2$	125.305	131.350
19	o-C_5H_4N	125.275	(131.561)/(131.870)
20	o,p-$C_6H_3(CF_3)_2$	125.045	131.060/131.085
21	o,o-$C_6H_3(CF_3)_2$	124.775	130.733
22	p-C_5NF_4	124.754	(131.065)
23	s-$C_6H_3(CF_3)_3$	124.208	130.146
24	o,o-$C_3H_3N_2$	123.774	(130.447)
25	p-$C_5H_4NCH_3^+$	123.222	129.319
26	s-$C_3H_2N_3$	123.178	(129.826)
27	p-$C_5H_4NH^+$	123.094	129.210
28	p-$C_5H_4O^+$	122.477	128.635

[a] B3LYP/6-311 + G(2d,p).

[b] Values in brackets do not correspond to the trend line depicted in Fig. 1.

the hydrogen atom with the basic nitrogen atom within the aromatic ring influences the C–N distance.

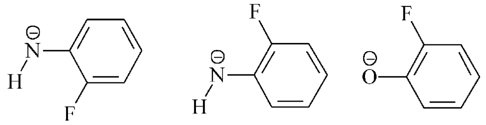


d(N-C): 131.561 pm (19-N$_{cis}$) 131.870 pm (19-N$_{tr.}$) d(O-C) 125.275 pm (19-O)

(5)

The deviation from the trend line which leads to longer C–N distances is differently pronounced. While the *cis* derivative (19-N$_{cis}$) is only slightly shifted, the *trans* derivative (19-N$_{trans}$) shows a significant deviation.

The data points belonging to aromatic groups with fluorine atoms in *ortho* position to the oxide or amide function also deviate significantly from the polynomial trend line in Fig. 1 (data points nos. 7, 10, 12, 15, 16 and 22). In principle this deviation could also be described by an electronic or steric interaction of the fluorine atoms with the hydrogen atom of the amide group which is absent in phenolate derivatives such as (7-O). Surprisingly, the C–N distances of the two o-C_6H_4F-$N(H)^-$ conformers (7-N$_{cis}$) and (7-N$_{trans}$), in which the N–H bond points into *cis* and *trans* direction relative to the fluorine atom, with values of 132.795 and 132.764 pm, respectively, are nearly equal. This means that the fluorine and the hydrogen atoms in the conformers (7-N$_{cis}$) and (7-N$_{trans}$) do not interact significantly. Therefore, the deviation of the data points for aromatic groups with fluorine atoms in *ortho* position from the trend line in Fig. 1 must be caused by a distinct different electronic or steric interaction of the fluorine atoms with the oxide and amide function, respectively.



d(N-C): 132.795 pm (7-N$_{cis}$) 132.764 pm (7-N$_{tr}$) d(O-C) 126.421 pm (7-O)

(6)

On the basis of these data, it is not possible – and not reasonable as discussed below – to answer the question which data set, the C–N or the C–O distances, is better suited to describe the electron withdrawing effect of aromatic groups with fluorine substituents or nitrogen ring atoms in the *ortho* positions.

The data points belonging to aromatic groups with two fluorine atoms or two nitrogen ring atoms in *ortho* position (data points nos. 26, 24, 22, 16, 15, 12 and 10) are in principle situated on a second trend line. This is shifted either to longer C–N or shorter C–O distances in relation to the already discussed trend line depicted in Fig. 1.

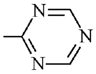
This demonstrates that the electronic nature of aromatic groups, classified by the C–E distances ($E = O^-$, NH^- and PH^-) of the corresponding phenolate, aryl amide or aryl phosphanide ions, is not directly comparable to each other. As a consequence, this model opens the possibility – as will be discussed below – to classify the electronic nature of substituents X in relation to any neutral or even charged group E.

The Hammett constants $\sigma_{m,p}$ for a given substituent X in *meta* or *para* position should be comparable with the differences of the C–E ($E = O^-$, NH^-) bond length of accordingly substituted compounds (XC_6H_4-E) and their non-substituted derivatives C_6H_5-E, Table 2.

$$\begin{aligned}\Delta(O^-)_{m,p} &= d(XC_6H_4\text{-}O^-)_{m,p} - d(C_6H_5\text{-}O^-)\\ \Delta(NH^-)_{m,p} &= d(XC_6H_4\text{-}NH^-)_{m,p} - d(C_6H_5\text{-}NH^-)\end{aligned} \qquad (7)$$

The calculation of these differences leads to the values $\Delta(O^-)$ and $\Delta(NH^-)$ which should be useful to classify the electronic effect of the substituents X at the corresponding phenolate or aryl amide ion. The resulting constants $\Delta(O^-)_{m,p}$ and $\Delta(NH^-)_{m,p}$ represent values to classify the electronic nature of the substituent X in relation to that of a hydrogen atom. A positive value indicates an electron withdrawing effect; a negative one classifies the corresponding substituent as an electron-donating group. Therefore, the values $\Delta(O^-)_{m,p}$ and $\Delta(NH^-)_{m,p}$ of a given substituent should be comparable with the corresponding Hammett constants $\sigma_{m,p}$. Table 2 exhibits generally corresponding tendencies of $\Delta(O^-)_{m,p}$ and $\Delta(NH^-)_{m,p}$ with the respective Hammett constants $\sigma_{m,p}$. The only exceptions in the given sequences are the values for *para* orientated fluorine atoms. The $\Delta(O^-)_p$ and $\Delta(NH^-)_p$ values of −0.13 and −0.23 pm, respectively, classify a *para* configured

Table 2
Hammett and modified Swain–Lupton constants [2] in relation to the corresponding $\Delta(E)_{m,p}$ values (pm) with E = O^-, NH^- and F

	CH_3	F	CF_3	CN	NO_2	*p* 
σ_m	−0.07	0.34	0.43	0.56	0.71	–
$\Delta(F)_m$ [a]	−0.12	0.37	0.44	0.57	0.68	
$\Delta(O^-)_m$ [b]	0.00	0.40	0.49	0.61	0.71	
$\Delta(NH^-)_m$ [c]	0.04	0.44	0.47	0.60	0.63	
σ_p	−0.17	0.06	0.54	0.66	0.78	–
$\Delta(F)_p$ [a]	−0.22	0.06	0.55	0.72	0.91	0.51
$\Delta(O^-)_p$ [b]	−0.09	−0.13	0.71	0.96	1.44	1.54
$\Delta(NH^-)_p$ [c]	−0.12	−0.23	1.03	1.27	1.76	1.82
R	−0.18	−0.39	0.16	0.15	0.13	–
F	0.01	0.45	0.38	0.51	0.65	–

[a] $\Delta(d(XC_6H_4\text{-}F)\text{-}d(C_6H_5\text{-}F))_{m,p}$ / pm.
[b] $\Delta(d(XC_6H_4\text{-}O^-)\text{-}d(C_6H_5\text{-}O^-))$ / pm.
[c] $\Delta(d(XC_6H_4\text{-}N(H)^-)\text{-}d(C_6H_5\text{-}N(H)^-))$ / pm.

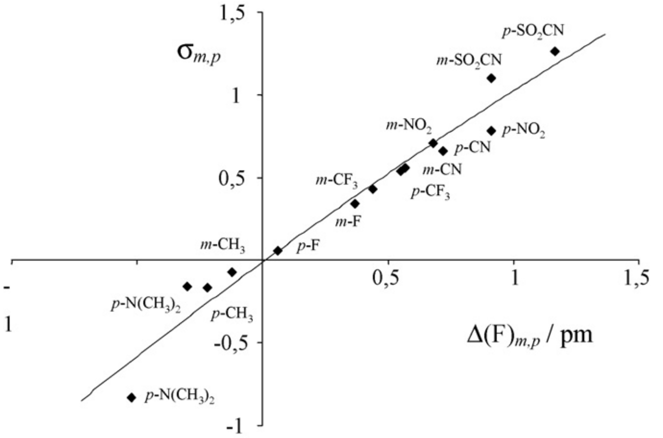


Fig. 2. Hammett constants ($\sigma_{m,p}$) vs. the corresponding $\Delta(F)_{m,p}$ values.

fluorine atom as an electron-donating group in relation to a hydrogen atom. This is a quite abnormal description of the electronic nature of a fluorine substituent. But as discussed below, it is correct in the case of a phenolate and aryl amide derivative.

The values of $\sigma_{m,p}$ represent the sum of resonance and field inductive effects. Swain and Lupton [13] introduced the variable *F* as a basis for separating the resonance and field inductive effects according to

$$F = a\sigma_m + b\sigma_p + c \tag{8}$$

where *a*, *b* and *c* are weighting factors [2]. To evaluate the resonance contribution *R* they made the assumption

$$\sigma_p = \alpha F + R \tag{9}$$

using a scaling factor α. As there has been some controversy on the values originally calculated by Swain and Lupton, Table 2 contains modified Swain–Lupton constants [2].

The values of *R* and *F* for a fluorine substituent are given in Table 2, classifying a fluorine atom as a π-donating (*R* −0.39) and σ-accepting (*F* 0.45) substituent. The values for σ_m are generally based on field inductive effects (*F*) while resonance effects (*R*) predominate the values for σ_p [2]. By this interpretation, the comparison of the σ_p value of 0.06 for a fluorine atom with the $\Delta(O^-)_p$ and $\Delta(NH^-)_p$ values of −0.13 and −0.23 pm, respectively, leads to the conclusion that the constants $\Delta(O^-)_p$ and $\Delta(NH^-)_p$ overestimate the resonance effect, the π-donation, of the fluorine atom. This can be explained by the strong π-donation of the oxide (O^-) as well as the amide ($N(H)^-$) function itself. The constants $\Delta(O^-)_{m,p}$ are referenced in relation to an O^- substituent with *F* and *R* values of −0.26 and −0.55, respectively [2]. The Hammett constants $\sigma_{m,p}$ are referenced in relation to a carboxylic acid/carboxylate function with *F* and *R* values of −0.10 and 0.10 for the COO^- unit. The strong π-donation of an O^- function causes a repulsive interaction with the π-donating fluorine atom, if they are connected via a *para* configured aromatic ring system. On the other side, a π-acidic carboxylic function supports the π-donation of a *para* orientated fluorine atom.

Due to the strong electron donating nature of the O^-, $N(H)^-$ and $P(H)^-$ function, their $\Delta(E)_{m,p}$ values exhibit only for electron-withdrawing groups the same tendency as the corresponding Hammett constants.

To obtain a better accordance even for electron-donating groups, it is reasonable to substitute the strongly π-donating O^- and $N(H)^-$ functions by a weaker π-donating substituent E as for example a fluorine atom. The $\Delta(F)_{m,p}$ values are in unusually good agreement with the corresponding Hammett values $\sigma_{m,p}$ which has to be accidentally (cf. Table 2). Due to the fact that the *F* and *R* values of a fluorine atom differ tremendously from those of a carboxylic acid/carboxylate function, a broader variation of the substituents X should exhibit a more significant deviation of $\Delta(F)_{m,p}$ from the corresponding Hammett constants. However, a plot of the Hammett constants ($\sigma_{m,p}$) versus the corresponding $\Delta(F)_{m,p}$ values including the strong electron withdrawing SO_2CN and the strong electron-donating $N(CH_3)_2$ group exhibits an unexpected good fit to the polinomial trend line shown in Fig. 2.

3. Conclusions

The electron withdrawing effect of a variety of differently substituted phenyl groups can be classified on the basis of the C–O or C–N distances of the corresponding phenolate or amide ions (Ar–O^- and Ar–NH^-), respectively, which are accessible by DFT calculations. An increasing electron withdrawing effect of the aromatic group leads to a shortened C–O and C–N distance of the corresponding ions. Within the presented model it is also possible to characterize the electronic nature of different types of six membered heterocycles.

This model is very useful to characterize the electronic nature of aromatic groups with different substituents or hetero ring atoms at the *meta* and *para* position relative to the amide or alcoholate function. It fails however, when aromatic groups with a fluorine substituent or a nitrogen ring atom in *ortho* position are considered.

The difference of the C–E distances of the substituted derivatives XC_6H_4-E and the non-substituted phenyl derivative,

C_6H_5-E, is defined by the value $\Delta(E)_{m,p}$. For E = O^-, NH^-, the values $\Delta(E)_{m,p}$ exhibit the same tendency as the corresponding Hammett constants. Therefore, the values $\Delta(E)_{m,p}$ are useful to classify the electron withdrawing effect of different kinds of phenyl substituents. The classification of the substituents X by the values of $\Delta(E)_{m,p}$ strongly depends on the nature of E. With the strongly π-donating groups E = O^- and NH^- a weakly π-donating fluorine atom in *para* position acts as an electron-donating group with respect to a hydrogen atom. In *para* position, resonance effects predominate field inductive effects. Changing into *meta* position, resonance effects can be neglected and a fluorine substituent acts as an electron withdrawing substituent in comparison to a hydrogen atom. The unusual classification of a *para* orientated fluorine atom as an electron donating substituent can be overcome using fluorobenzene as a reference substance. The resulting values of $\Delta(F)_{m,p}$ are in unexpectedly good agreement with the corresponding Hammett constants. Because the *R* and *F* values of a fluorine atom are different from those of a carboxyl and carboxylate function the obtained good agreement between $\Delta(F)_{m,p}$ and the corresponding Hammett constants must be accidentally.

Therefore, the values of $\Delta(F)_{m,p}$ which can be easily determined by DFT calculations are useful to classify the electronic nature of different kinds of substituents. The values $\Delta(E)_{m,p}$ do correspond with Hammett constants, but depending on the strong influence of the electronic nature of E on the interaction of the phenyl ring with the substituent X, they exhibit more or less deviations to the corresponding Hammett constants. Following this approach, the values $\Delta(E)_{m,p}$ open the possibility to classify the electronic nature of substituents X in relation to any neutral or even charged group E with at least one lone pair.

Acknowledgments

Dr. K. Glinka and Dr. W. Tyrra are acknowledged for helpful discussions. Prof. Dr. D. Naumann, Institute of Inorganic Chemistry at the University of Cologne, and Dr. N. Ignatiev, Merck KGaA Darmstadt, are acknowledged for their financial support.

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