

# SUBSTITUENT EFFECTS IN INFRARED SPECTROSCOPY. I. THE O-H STRETCHING FREQUENCIES IN MONOMERIC BENZOIC ACIDS

O. EXNER<sup>a</sup> and E. SVÁTEK<sup>b</sup>

<sup>a</sup> J. Heyrovský Institute of Polarography,  
Czechoslovak Academy of Sciences, Prague 1 and

<sup>b</sup> Research Institute of Pharmacy and Biochemistry, Prague 3

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The O-H stretching frequencies of sixty *meta*- and *para*-substituted benzoic acids have been measured in dilute tetrachloromethane solution. Their values are correlated by the Hammett equation with normal  $\sigma$  constants and slope  $\rho = -11.7 \text{ cm}^{-1}$  on the one hand, and by the equation (2) on the other hand; the validity of the latter for substituents without an  $\alpha$  lone electron pair has been thus confirmed even in the infrared spectroscopy. Somewhat lesser accuracy of the Hammett correlation is probably due to a different solvent than used in determining the  $\sigma$  constants; deviations of a systematic character have not been observed.

The dependence of characteristic infrared frequencies on substitution has been studied extensively. Qualitatively one can differentiate the frequencies little sensitive to substitution, those controlled mainly by the mass of the substituent, and those controlled by its polar properties<sup>1,2</sup>. The distinguishing of these categories is indeed qualified by the experimentally attainable accuracy. A relative independence of mass and combination effects can be anticipated especially in the case of stretching frequencies of terminal bonds in the molecule<sup>2</sup>, which can be correlated with quantities characterizing certain properties of the substituent. Such quantities can be *a*) the quantum-chemical indices<sup>3,4</sup>, *b*) constants derived empirically<sup>5-9</sup> from spectral data themselves, *c*) quantities determined from other experimental sources<sup>2,10</sup>, namely electronegativities<sup>2,3,11-13</sup> and reactivity constants<sup>14-23</sup>, denoted usually by the symbol  $\sigma$ .

In this series we intend to follow mainly the last mentioned approach. The characteristic infrared frequencies are considered as the most convenient physical quantity to be correlated with reactivity data since after multiplying by the Planck constant they afford quantities of the same type as reaction free energies or activation free energies<sup>16</sup>.

The process of stretching a bond and raising its vibrational energy bears a similarity with the initial phase of a chemical reaction, which results in its splitting. Nevertheless, it is out of question that no kind of  $\sigma$  constants can express all factors controlling the frequency. The purpose of the correlation is then to establish general regularities (interpretation of the slope of the correlation)

and to differentiate individual specific factors (analysis of deviations). In addition it was suggested to determine new constants  $\sigma$  from spectral measurements<sup>2,17</sup>, e.g. for sensitive substituents. Last but not least correlations can be helpful when the frequencies are assigned<sup>13,24</sup>.

Most often the Hammett equation has been used for correlations (see<sup>17,18</sup> and references quoted therein). When applied to infrared frequencies, it has the form (1) where  $\nu^0$  refers to the unsubstituted compound and  $\rho$  has the dimension  $\text{cm}^{-1}$ .

$$\nu = \nu^0 + \rho\sigma_{m,p} \quad (1)$$

Benzene derivatives, for which the Hammett equation holds, are advantageous since the mass effect can be usually neglected. However, the correlations described in the literature are often of low accuracy when compared to the experimental error<sup>17</sup>, as well as to the accuracy currently attained in reactivity correlations. As possible causes of the deviation one has to consider: a) Experimental errors can be considerable when compared to relatively small substituent effects, in the limiting case the assignment of the frequency can be wrong. b) The relative importance of inductive and mesomeric effects can differ with infrared frequencies and with reactivities. c) Frequencies can be affected by specific factors<sup>24,25</sup> as kinematic, combination and mass effects, which are not accounted for in constants  $\sigma$ . d) The solvents used are usually quite different when measuring the infrared spectra and when determining the  $\sigma$  constants.

The aim of several papers of this series is to estimate the above effects a) – d) by an empirical approach based on selected series of aromatic derivatives. These series must include derivatives of different kind, viz. *meta*- and *para*-substituted and with donor as well as with acceptor groups to evaluate effects under b), simple as well as complex substituents with regard to c) and interacting as well as non-interacting with solvents with regard to d). A practical lower limit of fifty derivatives is thus given, systematically chosen and measured under the same conditions in a single laboratory. The small number of derivatives studied (in average ten in the review<sup>17</sup>) was the main shortcoming of previous studies, namely *meta*-derivatives are usually less represented than *para*-derivatives and acceptor groups less than donor groups.

As a further diagnostic the equation derived by us previously<sup>26</sup> can serve, which related the effects of the same substituent on the positions *meta* and *para*. It is in principle independent of the Hammett equation but holds only for substituents without a lone electron pair in the  $\alpha$  position. For the infrared frequencies it has the form (2), the constant  $\lambda$  has been attributed an invariable value 1.14.

$$\nu_p - \nu^0 = \lambda(\nu_m - \nu^0) \quad (2)$$

The effect of substituents complying with this equation is predominantly an inductive one so that the deviations due to effects under b) are excluded. Moreover it can be anticipated that factors under d) and partially also c) cancel since they are similar with *meta*- and *para*-derivatives.

When choosing the reaction series, the reaction constant  $\rho$  should not be too small and the position and environs of the pertinent absorption band should allow to measure with a reasonable accuracy. With respect to all the requirements we chose for the first study the O—H stretching frequency in *meta*- and *para*-substituted benzoic acids. These compounds are of fundamental importance to the Hammett equation

TABLE I  
Infrared Hydroxyl Stretching Frequencies of Monomeric *meta*- and *para*-Substituted Benzoic Acids

Compound No	Substituent <sup>a</sup>	M.p., °C (corr.)	$\nu_{\text{OH}}$ , cm <sup>-1</sup> (in CCl <sub>4</sub> )	$\sigma_{m,p}$ <sup>a</sup>
1	H	122	3 539.0 <sup>b</sup>	0
2	3-CH <sub>3</sub>	111	3 540.2	-0.10
3	4-CH <sub>3</sub>	181	3 540.7	-0.15
4	3-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	111	3 539.7	-0.08
5	4-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	160	3 540.0	-0.09
6	3-CH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub>	123	3 538.1	0.06
7	4-CH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub>	216	3 538.6	0.07
8	3-CH <sub>2</sub> Cl	138	3 537.1	0.11
9	4-CH <sub>2</sub> Cl	205	3 537.0	0.12
10	3-CH <sub>2</sub> Br	153	3 537.7	0.12
11	4-CH <sub>2</sub> Br	229	3 537.7	0.14
12	3-CH <sub>2</sub> I	165	3 536.8	0.10
13	4-CH <sub>2</sub> I	235	3 537.3	0.11
14	3-CF <sub>3</sub>	104 <sup>c</sup>	3 533.6	0.46
15	4-CF <sub>3</sub>	218 <sup>c</sup>	3 532.6	0.53
16	3-CCl <sub>3</sub>	142	3 534.0	0.40
17	4-CCl <sub>3</sub>	198	3 533.0	0.46
18	3-C <sub>6</sub> H <sub>5</sub>	— <sup>d</sup>	3 537.3	0.06
19	4-C <sub>6</sub> H <sub>5</sub>	— <sup>d</sup>	3 538.8	0.03
20	3-COCH <sub>3</sub>	166 <sup>e</sup>	3 535.5	0.36
21	4-COCH <sub>3</sub>	207 <sup>e</sup>	3 535.3	0.44
22	3-COC <sub>6</sub> H <sub>5</sub>	164	3 534.8	0.34
23	4-COC <sub>6</sub> H <sub>5</sub>	197	3 534.3	0.42
24	3-COOCH <sub>3</sub>	192 <sup>f</sup>	3 535.6	0.36
25	4-COOCH <sub>3</sub>	220 <sup>f</sup>	3 535.5	0.43
26	3-CN	219	3 532.0	0.61
27	4-CN	218	3 530.3	0.69
28	3-NH <sub>2</sub>	174	3 541.2	-0.15
29	4-NH <sub>2</sub>	188	3 545.8	-0.66
30	3-N(CH <sub>3</sub> ) <sub>2</sub>	152	3 541.1	-0.20
31	4-N(CH <sub>3</sub> ) <sub>2</sub>	240	3 547.7	-0.82
32	3-N=NC <sub>6</sub> H <sub>5</sub>	171 <sup>g</sup>	3 536.0	0.30
33	4-N=NC <sub>6</sub> H <sub>5</sub>	248 <sup>g</sup>	3 535.7	0.34
34	3-NCS	— <sup>d</sup>	3 532.9	0.48
35	4-NCS	— <sup>d</sup>	3 535.1	0.38
36	3-N <sub>3</sub>	161	3 535.5	0.27
37	4-N <sub>3</sub>	184	3 537.6	0.15
38	3-NO <sub>2</sub>	142	3 530.9 <sup>h</sup>	0.70
39	4-NO <sub>2</sub>	240	3 530.0 <sup>h</sup>	0.80
40	3-OH	202	3 537.5	0.09

TABLE I  
 (Continued)

Compound No	Substituent <sup>a</sup>	M.p., °C (corr.)	$\nu_{\text{OH}}$ , $\text{cm}^{-1}$ (in $\text{CCl}_4$ )	$\sigma_{\text{m,p}}$ <sup>a</sup>
41	4-OH	214	— <sup>j</sup>	—0.33
42	3-OCH <sub>3</sub>	106	3 538.9	0.12
43	4-OCH <sub>3</sub>	182	3 542.7 <sup>k</sup>	—0.26
44	3-OC <sub>2</sub> H <sub>5</sub>	— <sup>d</sup>	3 538.7	0.13
45	4-OC <sub>2</sub> H <sub>5</sub>	— <sup>d</sup>	3 543.0	—0.25
46	3-OC <sub>6</sub> H <sub>5</sub>	— <sup>d</sup>	3 534.6	0.26
47	4-OC <sub>6</sub> H <sub>5</sub>	— <sup>d</sup>	3 536.6	0.14 <sup>l</sup>
48	3-OCOCH <sub>3</sub>	132	3 537.0	0.26
49	4-OCOCH <sub>3</sub>	188	3 538.2	0.16
50	3-OCOC <sub>6</sub> H <sub>5</sub>	144	3 537.2	0.21
51	4-OCOC <sub>6</sub> H <sub>5</sub>	224	3 538.5	0.13
52	3-OSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	116	3 534.7	0.36
53	4-OSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	170	3 536.5	0.33
54	3-SO <sub>2</sub> F	— <sup>d</sup>	3 528.1	0.80 <sup>f</sup>
55	4-SO <sub>2</sub> F	— <sup>d</sup>	3 526.4	0.91 <sup>f</sup>
56	3-F	124	3 536.1	0.36
57	4-F	181	3 538.2	0.05
58	3-Cl	156	3 535.2	0.38
59	4-Cl	241	3 536.5 <sup>m</sup>	0.23
60	3-Br	155	3 534.3	0.39
61	4-Br	255	3 535.5	0.23
62	3-I	186	3 534.0	0.34
63	4-I	270	3 536.2	0.19

<sup>a</sup> Most of the compounds were described in previous communications<sup>26,30</sup> where the  $\sigma$  constants used are also discussed; <sup>b</sup> literature<sup>19,28,29</sup> gives the values 3541, 3536 and 3551  $\text{cm}^{-1}$ , resp.; <sup>c</sup> these acids were prepared by hydrolysis of the nitriles obtained from the corresponding amines; the products were in accord with literature data<sup>31</sup>; <sup>d</sup> these compounds were kindly supplied to us by Prof. W. Palaczko, Warszawa (substituent C<sub>6</sub>H<sub>5</sub>), Prof. K. Antoš, Bratislava (substituent NCS), Dr K. Kalfus, Pardubice (substituents OC<sub>2</sub>H<sub>5</sub> and OC<sub>6</sub>H<sub>5</sub>), and Dr R. Pollet, Antwerp (substituent SO<sub>2</sub>F); <sup>e</sup> these acids were prepared by hydrolysis of the corresponding nitriles<sup>32</sup>; <sup>f</sup> see ref.<sup>33</sup>; <sup>g</sup> prepared according to ref.<sup>34</sup>; <sup>h</sup> literature<sup>19,27-29</sup> gives the values 3531, 3528, 3528 and 3548  $\text{cm}^{-1}$  for the *meta*-isomer and 3531, 3527, 3527 and 3541  $\text{cm}^{-1}$  for the *para*-isomer; <sup>j</sup> non-soluble in tetrachloromethane; <sup>k</sup> in the literature<sup>19,28,29</sup> the values 3545, 3541, and 3560  $\text{cm}^{-1}$  are given; <sup>l</sup> a fully reliable value for this constant does not exist, the value given<sup>30</sup> is based on measurement of Wepster<sup>35</sup>; <sup>m</sup> literature<sup>19,27-29</sup> gives the values 3539, 3537, 3535 and 3551  $\text{cm}^{-1}$ , resp.

since they served to define the constants  $\sigma$ . The frequency chosen is also advantageous for the reason that the small mass of the hydrogen atom unable to abandon the mass effect. In addition the position of the band makes it possible to work in dilute solutions where the compounds studied are present in the monomeric form; in this way the necessary accuracy is warranted. In previous studies<sup>19,27-29</sup> this accuracy was not quite satisfactory, moreover the number of derivatives was insufficient (at best 19 in ref.<sup>19</sup>), substituents of all types being not included proportionally. The only shortcoming of our series of derivatives is the insufficient solubility of some important members in tetrachloromethane whereas another suitable solvent was not found. Anyhow, we have been able to comply with the required number of fifty derivatives.

### EXPERIMENTAL AND RESULTS

*Substances used.* Most of the *meta*- and *para*-substituted benzoic acids were characterized in the preceding communications<sup>26,30</sup>. The remaining ones were either commercial products or their preparation is mentioned in the footnotes to Table I.

*Spectral measurements.* The infrared absorption spectra in the region 3400–3700  $\text{cm}^{-1}$  were scanned in tetrachloromethane solutions of the concentration c.  $10^{-3}\text{M}$  in 3 cm "infrasil" cells. The instrument Unicam SP 700 was calibrated using the peak of water vapour at 3566  $\text{cm}^{-1}$ . The measured frequencies are listed in Table I, their accuracy is estimated from repeated measurements to  $\pm 0.3 \text{ cm}^{-1}$  (standard deviation).

The agreement of our results with literature data<sup>19,27-29</sup> is satisfactory and is illustrated on several examples in the footnotes to Table I. The discrepancies are due mainly to calibration, our figures being c.  $2 \text{ cm}^{-1}$  lower than those of Lloyd and co-authors<sup>19</sup> and c.  $2 \text{ cm}^{-1}$  higher than those of Peltier<sup>27</sup> or Goulden<sup>28</sup>, the data of Flett<sup>29</sup> being outside.

### DISCUSSION

The first task is to verify the equation (2), derived from reactivities, on infrared spectral frequencies. In Fig. 1 the substituent shifts of the OH stretching frequencies are plotted against each other, the direction of the axes was chosen so that to place electron attracting substituent on the right-hand side as in the correlations of dissociation constants. The pertinent statistics are given in Table II. The plot presents the same picture as the reactivity correlations<sup>26,30</sup>: Sixteen points for substituents without a lone electron pair are situated near the straight line with the expected slope 1.14, the remaining ones deviate downwards from this line.

The statistical treatment is somewhat different from a common linear regression (see<sup>33</sup>). The constant  $\lambda = 1.150$ , computed for sixteen mentioned points, does not differ significantly from the usual value<sup>26</sup>, the standard deviation  $s$  shows that the relation holds practically within experimental error. The meaning of the correlation coefficient is also somewhat different, however, its value is unusually high. We showed

previously<sup>26,30,33</sup> that the equation (2) is one of the best experimentally supported relationships.

Equation (2) was interpreted<sup>26</sup>, supposing that substituents without an  $\alpha$  lone electron pair are not appreciably conjugated with the benzene nucleus, their effect being essentially inductive in nature. The deviations of substituents with an  $\alpha$  electron pair (including the phenyl group) from the line can serve as a measure of their mesomeric effect<sup>30</sup>. Their "isovalent" conjugation<sup>36</sup> is evidently much stronger than the "sacrificial" conjugation of the acceptor groups as  $\text{NO}_2$ , CN, COR or the hyperconjugation of groups  $\text{CF}_3$  and  $\text{CCl}_3$ .

From Fig. 1 the conclusion can be drawn that the conjugation of acceptors with the benzene nucleus is not manifested significantly in infrared frequencies. In the same way as with reactivities this conclusion is limited by the precondition that not even the reaction centre has an  $\alpha$  electron pair. On the other hand the presence of the carboxyl group, which is also an acceptor, can weaken the conjugation of another acceptor. For the time being, it remains undecided how strong is and how is manifested the conjugation in simple monoderivatives, *e.g.* in nitrobenzene.

The constant  $\lambda$  in equation (2) cannot be *a priori* presumed to be solvent-independent. The independency follows only from the simultaneous and exact validity of both equations (1) and (2). Empirically a constant value  $\lambda$  was found in aqueous dioxan of various concentration<sup>33</sup>; Fig. 1 shows the same value even in a nonpolar solvent. It can be concluded that solvent effects are neither essential for the validity of equation (2) nor violate it significantly.

TABLE II  
Statistics of the Correlation of the O—H Frequency in Substituted Benzoic Acids

Quantity	Equation (1)	Equation (1), solvent-insensitive substituents only	Equation (2)
$\rho$ , $\text{cm}^{-1}$	$-11.74 \pm 0.33$	$-11.44 \pm 0.55$	—
$\nu^0$ , $\text{cm}^{-1}$	$3\,539.04 \pm 0.12$	$3\,538.84 \pm 0.15$	(3 539.0)
$\lambda$	—	—	$1.150 \pm 0.019$
$r^a$	$-0.9776$	$-0.9789$	0.9976
$s^b$ , $\text{cm}^{-1}$	$0.784^d$	$0.513^d$	$0.374^d$
$f^c$	60	19	14

<sup>a</sup> Correlation coefficient; <sup>b</sup> Standard deviation from the regression line; <sup>c</sup> Degrees of freedom;

<sup>d</sup> The ratio of standard deviations for the first and second column is significant at the level  $\alpha = 0.025$ , for the second and the third column at  $\alpha = 0.12$ , and for the first and the third highly significant at  $\alpha = 0.005$  (F-test).

The Hammett plot of our experimental data is shown in Fig. 2. Normal constants  $\sigma_m$  and  $\sigma_p$  were used, which had been derived essentially from dissociation constants of benzoic acids with but insignificant corrections<sup>26</sup> and can be rightly used for the same compounds with the same position of the reaction centre. Rao and Venkataraman<sup>17</sup> preferred the  $\sigma^+$  constants, expressing a stronger mesomeric effect of donors. This is neither warranted theoretically, nor experimentally proved since the difference of standard deviations<sup>17</sup> is insignificant with six derivatives only. Our data give no reason to search for other kind of constant  $\sigma$ , neither generally nor for some substituents only.

The statistics of the Hammett correlation are given in Table II. Our value of  $\rho$  is in reasonable agreement with previous estimates<sup>17,27</sup>, in the latter case the lower absolute value of  $\rho$  was due to the presence of *ortho*-derivatives in the correlation<sup>27</sup>.

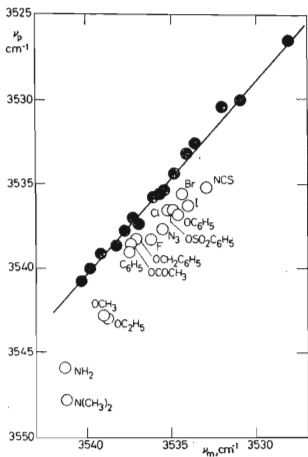


FIG. 1

The Dependence of Relative Values  $\nu_{\text{O-H}}$  of Benzoic Acids Substituted in the *meta* ( $x$  axis) and *para* ( $y$  axis) Positions

Substituents without ( $\circ$ ) and with ( $\bullet$ ) an  $\alpha$  lone electron pair are shown, the straight line has the slope 1.14 expected according to Eq. (2).

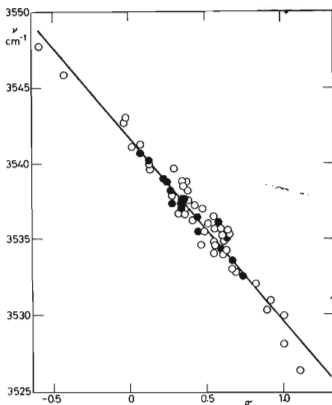


FIG. 2

Hammett Plot of the O—H Stretching Frequency of Substituted Benzoic Acids

$\bullet$  Solvent-insensitive <sup>41</sup>substituents,  
 $\circ$  other substituents.

Noteworthy is the small difference against the  $\rho$  constant for the OH frequency of substituted phenols<sup>17,28,37,38</sup>, which is one atom nearer to the substituent. The concept of the successive attenuation of substituent effects with each bond (the so-called transmission factor<sup>26</sup>) cannot be probably applied to infrared frequencies without change.

The interpretation of the sign of  $\rho$  is not quite simple in the case of infrared frequencies. The explication based on rehybridization supposes that the bond to an electron attracting substituents acquires less *s*-character and the remaining bonds more *s*-character so that their force constants increase<sup>39</sup>. Accordingly  $\rho$  should be positive, at least for simple valence stretching vibrations what is not in agreement with facts, neither generally<sup>17</sup> nor in the special case of the OH frequency. The explication operating with mesomeric structures was used with phenols<sup>38</sup> but cannot be applied generally, especially to aliphatic derivatives<sup>28</sup>. We believe the natural polarity of the vibrating bond to be an important factor. If the negative pole is oriented towards the substituent (O—H, N—H), the polarity is enhanced and the force constant reduced by electron attracting substituents;  $\rho$  is then negative. If the positive pole is nearer to the substituent (C=N, C=O) the polarity is reduced by electron attracting substituents and  $\rho$  is positive. In addition to the effect on the force constant, the substituent effects on valence angles come doubtless into play<sup>39</sup>, especially with more complex vibrations (NO<sub>2</sub> asym, NH<sub>2</sub> sym, NH<sub>2</sub> asym).

The scatter of points in Fig. 2, expressed by the standard deviation 0.784 cm<sup>-1</sup> is distinctly less than in correlations in ref.<sup>17</sup>, but larger than the supposed experimental error. According to the correlation coefficient the correlation is worse than it is usual with good reactivity data and can be denoted as "satisfactory"<sup>40</sup>. We deduce that the experimental inaccuracy combined with the small number of derivatives was one cause of the lower accuracy in correlation of infrared frequencies<sup>17</sup>, but not the only one. In our case the ratio of the experimental error to the range of values is 1 : 50, approximately the same as in good measurements of dissociation constants or kinetics.

When the scatter in Fig. 2 is compared to the relatively higher accuracy in Fig. 1, the most probable explanation is the solvent effect, which can be anticipated similar in both positions and is, therefore, not manifested by deviations from equation (2). This conclusion can be further tested by choosing only substituents with but a small interaction with solvent. According to fluorine NMR shifts the substituents CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, CF<sub>3</sub>, CCl<sub>3</sub>, CH<sub>2</sub>Cl, CH<sub>2</sub>Br, F, Cl and Br (represented by full points in Fig. 2) can be considered to be inert<sup>41</sup>. The result of the test (Table II) is not quite conclusive, also owing to a small number of these substituents and same uncertain values of  $\sigma$ ; nevertheless the correlation has been improved. Further argument can be seen in big deviations of some especially solvent-sensitive substituents (OR, COCH<sub>3</sub>, SO<sub>2</sub>F). What is observed, is in fact the difference between solvent effects in tetrachloromethane and water. Certain dependence of  $\sigma$  constants



on solvent has been already observed. Taft suggested two  $\sigma$  values for hydroxylic and non-hydroxylic solvents with acceptor substituents in the *para* position and for OH and OCH<sub>3</sub> groups in both positions<sup>42</sup>. In Fig. 2 the deviations of some acceptor groups are not confined to the *para*-position, however, the use of Taft's values for non-hydroxylic solvents would reduce the deviations in most cases.

On the other hand, Fig. 2 does not give evidence of specific effects, which should play a role only in infrared frequencies and violate thus their correlation with reactivity data. Especially no deviations of *meta*-derivatives are seen in Fig. 2, which were observed with the C≡N stretching frequency in substituted benzonitriles<sup>25</sup> and anti-symmetric frequency of the NO<sub>2</sub> group in substituted nitrobenzenes<sup>43</sup>. Although we have no theoretical explanation of this phenomenon for the time being, we see the main difference between the two types in the longer distance of the O—H bond from the benzene ring bearing the substituent.

As far as the pure mass effect of the substituent is considered, we can compare the four *meta*-halogen derivatives with roughly equal polar substituent effects. For substituents F, Cl, Br and I the corresponding reduced mass  $\mu$  equals 1.0007, 1.0015, 1.0029 and 1.0038, respectively. Accordingly, the frequencies of the chloro-, bromo- and iodo-derivative should be 1.2, 3.7 and 5.4 cm<sup>-1</sup> lower than that one of the fluoro-derivative. The experimental values 0.9, 1.8 and 2.1 cm<sup>-1</sup>, respectively, are in the right order but less than a half. The computation of the reduced mass is, of course, not justified with complex molecules. However, it is clear that the pure mass effect cannot be completely neglected even in the case of the O—H bond.

To conclude we believe that infrared spectral data can be correlated with reactivity parameters after a careful analysis of individual cases, based on the study of a great number of derivatives. We do not consider feasible to estimate the values of dissociation constants<sup>28</sup> or  $\sigma$  constants<sup>17</sup> from these correlations, the values obtained could be valid for non-polar solvents at best. On the other hand, we do not agree to the opinion<sup>18</sup> that the substituent effects in infrared spectroscopy can be discussed only qualitatively in rough lines.

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