Supplementary Material (ESI) for New Journal of Chemistry

Range of validity of the Hammett equation: acidity of substituted ethynylbenzenes

Stanislav Böhm,[a] Patrik Pařík[b] and Otto Exner[*,c]

[a] *Institute of Organic Chemistry, Prague Institute of Chemical Technology, CZ-16628 Praha 6, Czech Republic*
[b] *Department of Organic Chemistry, Faculty of Chemical Technology, University of Pardubice, CZ-53210 Pardubice, Czech Republic*
[c] *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, CZ-16610 Praha 6, Czech Republic*

Supplementary information

Table S1 Calculated energies and conformations of substituted phenylacetic acids **2a** and **2b**

	Substituent	Conformation[a]	*E* acid a. u.	*E* anion a. u.
2a	3-CF_3		–795.4357483	–794.8901097
2b	3-CHO	*ap*	–572.0588915	–571.5132865
		sp	–572.0586928	–571.5113821
		effective values	–572.0588025	–571.5130628

[a] Conformation on the C3–C(O) bond of the substituent is given in this column. Conformation on the C1–C(H_2) bond is uniform in all derivatives, with the C(H_2)–C(OOH) bond almost perpendicular to the ring plane as in ref. 18.

Table S2 Calculated energies and conformations of some substituted benzylalcohols **3a** – **3e**

	Substituent	alcohol		anion	
		Conformation[a]	*E* a. u.	Conformation[b]	*E* a. u.
3a	H	-. *ap*	–346.059675	–	–345.4600218
		-, *sp*	–346.061358		
		effective value	–346.061115		
3b	3-CH_3	*ap, ap*	–385.285278	*ap*	–384.6846218
		ap, sp	–385.287095		
		sp, ap	–385.285367	*sp*	–384.6849769
		sp, sp	–385.287202		

Table S2 continued

		effective value	–385.286921	effective value	–384.6848323
3c	3-CF_3	*ap, ap*	–682.682721	*ap*	–682.0944002
		ap, sp	–682.683786		
		sp, ap	–682.682603	*sp*	–682.0937031
		sp, sp	–682.683618		
		effective value	–682.683449	effective value	–682.0941748
3d	3-CHO	*ap, ap, ap*	–459.199590	*ap, ap*	–458.6119344
		ap, ap, sp	–459.200019	*ap, sp*	–458.6102180
		ap, sp, ap	–459.200596		
		ap, sp, sp	–459.200987		
		sp, ap, ap	–459.199841	*sp, ap*	–458.6119125
		sp, ap, sp	–459.199060	*sp, sp*	–458.6070889
		sp, sp, ap	–459.200711		
		sp, sp, sp	–459.200085		
		effective value	–459.200443	effective value	–458.6117811
3e	3-OH	*ap, ap, ap*	–421.182345	*ap, ap*	–420.5822315
		ap, ap, sp	–421.182102	*ap, sp*	–420.5839546
		ap, sp, ap	–421.184112		
		ap, sp, sp	–421.183854		
		sp, ap, ap	–421.182367	*sp, ap*	–420.5822875
		sp, ap, sp	–421.183229	*sp, sp*	–420.5874096
		sp, sp, ap	–421.184015		
		sp, sp, sp	–421.184631		
		effective value	–421.184013	effective value	–420.5872809

[a] The conformations are given in the sequence: first on the C1–C(H_2) bond, second on the C–O bond of the CH_2OH group, third on the C–C or C–O bond of the substituent. [b] The conformation are given first on the C1–C(O) of the CH_2OH group, second on the C–C or C–O bond of the substituent.

Table S3 Calculated reaction energies of acidobasic reactions of benzene derivatives with *meta* substituents (in kJ mol^{-1}): source matrix for testing the Hammett equation[a]

Acid / Substituent	$ArCO_2H$	$ArCH_2CO_2H$	$ArCH_2OH$	$ArC{\equiv}CH$	$ArOH$	$ArCNH^+$	$ArCO_2H_2^-$	$ArNO_2H^+$
H	0	0	0	0	0	0	0	0
3-CH_3	3.39	6.28	2.61	2.94	2.93	–9.16	–8.64	–11.47
3-CF_3	–32.96	–24.44	–31.03	–32.37	–42.68	27.23	30.00	30.17
3-CHO	–34.53	–24.17	–32.64	–32.36	–40.17	19.73	20.22	22.95
3-CN	–43.76	–28.87	–45.61	–42.53	–58.99	37.22	41.76	40.84
3-NH_2	6.53	6.28	3.35	6.14	6.69	–16.55	–18.61	–24.02
3-NO_2	–48.04	–30.96	–43.51	–46.59	–63.60	41.15	44.52	45.76
3-OH	–8.69	–4.60	–11.45	–7.43	–8.37	–0.92	–1.18	–1.84
3-F	–18.58	–8.37	–16.32	–18.36	–22.59	18.34	19.60	19.95
3-Cl	–22.85	–10.04	–20.08	–22.42	–31.38	15.76	17.55	16.38

[a] Ref. 17,18,23-25 and this work.

Table S4 Calculated reaction energies of acidobasic reactions of benzene derivatives with *para* substituents (in kJ mol^{-1}): source matrix for testing the Hammett equation[a]

Acid / Substituent	$ArCO_2H$	$ArCH_2CO_2H$	$ArCH_2OH$	$ArC{\equiv}CH$	$ArOH$	$ArCNH^+$	$ArCO_2H_2^-$	$ArNO_2H^+$
H	0	0	0	0	0	0	0	0
4-CH_3	5.51	9.62	6.28	5.75	5.44	–14.68	–15.88	–20.95
4-CF_3	–35.95	–20.50	–30.12	–40.30	–51.46	29.85	32.86	32.36
4-CHO	–36.17	–21.34	–30.12	–49.49	–66.53	24.31	25.80	24.34
4-CN	–46.72	–31.38	–42.26	–54.23	–70.71	36.56	40.26	36.48
4-NH_2	18.52	11.72	11.30	19.39	15.90	–50.04	–54.55	–74.95
4-NO_2	–54.49	–34.73	–46.02	–70.76	–87.03	46.07	50.37	50.20
4-OH	4.40	3.77	0.42	7.40	8.37	–19.17	–20.28	–31.13
4-F	–13.60	–6.69	–11.72	–10.32	–10.04	8.80	10.63	6.21
4-Cl	–19.73	–9.62	–18.83	–19.09	–25.10	7.46	8.71	1.20

[a] Ref. 17,18,23-25 and this work.

Table S5 Calculated reaction energies of isodesmic reactions of uncharged benzene derivatives, with *meta* substituents (in kJ mol^{-1}): source matrix for testing the Hammett equation[a]

Substituent / Substituent	COOH	CN	C≡CH	NH_2	$N(CH_3)_2$	NO_2	OH	SH
H	0	0	0	0	0	0	0	0
3-CH_3	–0.73	–1.60	–0.37	0.00	0.42	0	–2.02	–0.42
3-CF_3	5.40	9.72	3.65	–2.09	–4.60	10.93	–0.42	2.09
3-CHO	4.24	8.16	3.1	–2.93	–5.02	9.93	–8.37	2.09
3-CN	6.81	12.42	4.55	–2.93	–5.44	14.36	–0.42	2.93
3-NH_2	–1.04	–2.52	–0.6	0.00	0.00	–1.14	0.00	–0.84
3-NO_2	7.80	14.36	5.24	–3.35	–7.11	16.85	–2.09	3.35
3-OH	0.51	1.37	0.65	–2.09	–2.51	2.20	0.42	–0.42
3-F	3.73	6.27	2.31	–1.67	–3.76	7.62	0.84	1.26
3-Cl	4.13	6.60	2.47	–1.67	–3.35	8.11	0.84	1.26

[a] Ref. 17,22,23,25 and this work.

Table S6 Calculated reaction energies of isodesmic reactions of uncharged benzene derivatives with *para* substituents (in kJ mol^{-1}): source matrix for testing the Hammett equation[a]

Substituent / Substituent	COOH	CN	C≡CH	NH_2	$N(CH_3)_2$	NO_2	OH	SH
H	0	0	0	0	0	0	0	0
4-CH_3	–2.47	–2.74	–0.97	2.51	2.51	–3.62	1.67	0.42
4-CF_3	6.01	9.27	3.10	–6.69	–9.20	10.82	–0.84	–0.42
4-CHO	6.17	7.95	1.31	–12.13	–14.64	10.31	–8.79	–3.35
4-CN	6.58	10.82	2.84	–9.62	–12.97	13.16	–1.26	–0.84
4-NH_2	–10.29	–9.36	–3.80	10.88	10.88	–12.50	7.11	0.84
4-NO_2	8.61	13.16	2.90	–13.39	–17.99	16.79	–1.26	–2.09
4-OH	–5.43	–3.51	–1.26	8.79	8.37	–5.22	6.69	2.51
4-F	0.02	3.09	1.40	5.02	4.60	3.28	5.86	3.77
4-Cl	1.35	4.22	1.50	1.26	–0.42	4.73	2.51	1.67

[a] Ref. 17,22,23,25 and this work.

Fig. S1 Tree diagram displaying results of cluster analysis (Furthest Neighbour method) applied to the matrix meta/para in the set **A**