JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 11, 437–447 (1998)

A new approach to the theoretical estimation of inductive constants

A. R. Cherkasov,* V. I. Galkin and R. A. Cherkasov

Kazan State University, Kazan 420008, Russia

Received 15 April 1997; revised 28 September 1997; accepted 15 October 1997

ABSTRACT: A new model of the inductive effect is proposed, allowing highly accurate theoretical calculations of inductive constants for a diversity of substituents, using a simple and readily available system of mathematics. According to this approach, the inductive effect of a substituent is considered in terms of the additive influence of its constituent atoms. A constant inherent capacity for inductive interaction with a reactive center (with a four-coordinate carbon atom chosen for such a center), represented by an atomic constant σ_A, is ascribed to each atom. Values of σ_A for a wide variety of atoms are determined, and their physical meaning is revealed to elucidate to a certain extent the physical nature of the inductive effect. In addition, the proposed model permits the convenient use in calculations of group constants σ_G characterizing the inductive power of groups. Values of σ_G are determined for molecular fragments that are most widely dealt with in organic chemistry, and the use of σ_A or σ_G constants and of their superposition is shown to have, in most cases, little or no effect on the accuracy and reproducibility of the results obtained. It is also shown that, in terms of the developed approach, the inductive effect of a substituent is closely associated with its conformation. Theoretical inductive constants were calculated for 427 organic, aromatic, organometallic and charged substituents, and they showed perfect correlation with the corresponding experimental values. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: inductive constants; theoretical estimation

INTRODUCTION

The relationship between the structure of organic and organoelement compounds and their reactivity is one of the fundamental problems of contemporary chemistry. At present, the overall interaction of a substituent with a reactive center is conventionally subdivided into inductive, mesomeric and steric components; the impossibility of isolating each of these correctly is nowadays one of the main obstacles to the further development of quantitative organic chemistry and correlation analysis.

Our experience accumulated in studying steric effects[1] indicates very high efficiency of modeling as a method for quantitatively evaluating the substituent effect. For example, our model of the frontier steric effect[1–3] enabled us not only to calculate adequately and with high accuracy the steric effect of any substituent at any reaction center, but also to solve many other problems that are intractable or hard to solve in terms of the existing empirical scales. Extensive testing of the model on a great variety (hundreds) of organic reaction series has revealed no restrictions on the applicability of this approach.

In the present work, we made an attempt to develop a relatively simple model of the inductive effect which, being based on an available body of mathematics, would allow sufficiently adequate theoretical calculations of inductive constants for a wide variety of organic and organoelement substituents and, to a certain extent, elucidate the nature of inductive interactions.

MODEL OF THE INDUCTIVE EFFECT

Inductive effect of organic substituents

The following main postulates and assumptions constitute the basis of the developed approach:[4,5]

1. Each atom, depending on its chemical nature and valence state, possesses an intrinisic inductive power. For the above reasons it is appropriate to choose as a measure of this ability not one of the already known physical parameters such as electronegativity or dipole moment, but a certain empirical quantity (designated σ_A) referenced to one of the currently used empirical inductive scales, taken as a basis.
2. We chose the Taft inductive scale[6] as such a basic scale and extended it to the utmost limit by re-calculating the missing constants of one or another

---

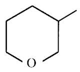
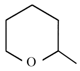
*Correspondence to: A. R. Cherkasov, Kazan State University, Kazan 420008, Russia.

CCC 0894–3230/98/070437–11 $17.50

Table 1. Experimental and theoretical [calculated with Eqn (2)] inductive Taft's σ^* constants of organic substituents

No.	Substituent	σ^*	$\sigma_{\text{theor.}}^*$
1	—F	3.21 ± 0.17	3.08
2	—CH_2F	1.10 ± 0.17	1.27
3	—Cl	2.89 ± 0.17	2.43
4	—CH_2Cl	0.96 ± 0.17	1.08
5	—$CHCl_2$	1.95 ± 0.17	2.16
6	—$CHClCH_3$	0.83 ± 0.17	1.08
7	—$CHClC_2H_5$	0.94 ± 0.10	1.08
8	—C_2H_4Cl	0.30 ± 0.07	0.50
9	—$CH_2CHClCH_3$	0.24 ± 0.10	0.49
10	—Br	2.80 ± 0.17	2.36
11	—CH_2Br	1.15 ± 0.17	1.14
12	—$CHBrCH_3$	1.09 ± 0.17	1.14
13	—$CHBrC_2H_5$	0.91 ± 0.10	1.14
14	—$CHBr_2$	1.97 ± 0.17	2.28
15	—$CHBrCH_2Br$	1.33 ± 0.10	1.62
16	—C_2H_4Br	0.17 ± 0.07	0.48
17	—$CH_2CHBrCH_3$	0.25 ± 0.10	0.51
18	—I	2.38 ± 0.17	2.00
19	—CH_2I	0.96 ± 0.17	1.23
20	—C_2H_4I	0.21 ± 0.10	0.39
21	—OH	1.60 ± 0.17	1.58
22	—OCH_3	1.79 ± 0.17	1.63
23	—OC_2H_5	1.68 ± 0.17	1.63
24	—OC_3H_7 (*n*)	1.68 ± 0.17	1.63
25	—OC_3H_7 (*i*)	1.61 ± 0.17	1.63
26	—OC_4H_9 (*n*)	1.68 ± 0.17	1.63
27	—OC_4H_9 (*sec*)	1.65 ± 0.17	1.63
28	—OC_5H_{11} (*n*)	1.55 ± 0.10	1.63
29	—OC_5H_{10} (*cyc*)	1.61 ± 0.17	1.63
30	—$OC_2H_4CHMe_2$	1.55 ± 0.17	1.63
31	—OCH_2CMe_3	1.54 ± 0.17	1.63
32	—$OCHCH_3CMe_3$	1.48 ± 0.17	1.63
33	—OC_6H_{12} (*cyc*)	1.88 ± 0.17	1.63
34	—CH_2OH	0.56 ± 0.17	0.54
35	—CH_2OCH_3	0.56 ± 0.10	0.54
36	—$CH(OCH_3)_2$	1.12 ± 0.17	1.08
37	—$CH_2OC_3H_7$ (*i*)	0.59 ± 0.11	0.54
38	—$CH_2OC_3H_7$ (*n*)	0.61 ± 0.11	0.54
39	—C_2H_4OH	0.23 ± 0.17	0.22
40	—$C_2H_4OCH_3$	0.16 ± 0.17	0.22
41	—$C_2H_4OC_2H_5$	0.23 ± 0.17	0.22
42	—SH	1.61 ± 0.17	1.52
43	—SCH_3	1.66 ± 0.17	1.55
44	—SC_2H_5	1.55 ± 0.17	1.55
45	—SC_3H_7 (*n*)	1.48 ± 0.17	1.55
46	—SC_3H_7 (*i*)	1.55 ± 0.17	1.55
47	—SC_4H_9 (*n*)	1.55 ± 0.17	1.55
48	—SC_4H_9 (*sec*)	1.48 ± 0.17	1.55
49	—CH_2SH	0.63 ± 0.17	0.63
50	—CH_2SCH_3	0.63 ± 0.10	0.63
51	—$CH_2SC_3H_7$ (*n*)	0.54 ± 0.10	0.63
52	—$CH_2SC_3H_7$ (*i*)	0.57 ± 0.10	0.63
53	—$CH_2SC_4H_9$ (*n*)	0.57 ± 0.10	0.63
54	—C_2H_4SH	0.19 ± 0.10	0.26
55	—$CH = CH_2$	0.40 ± 0.17	0.42
56	—$CH = CHCH_3$	0.30 ± 0.17	0.42
57	—$C(CH_3) = CH_2$	0.50 ± 0.17	0.42
58	—$CH{=}CHC_2H_5$	0.32 ± 0.17	0.42
59	—NH_2	0.72 ± 0.17	0.82
60	—$NHCH_3$	0.69 ± 0.12	0.85
61	—NHC_2H_5	0.96 ± 0.12	0.83
62	—$N(CH_3)C_2H_5$	0.83 ± 0.12	0.83
63	—$N(C_2H_5)_2$	0.86 ± 0.12	0.83
64	—CH_2NH_2	0.50 ± 0.12	0.29
65	—$CHCH_3NHCH_3$	0.01 ± 0.12	0.29
66	—$CH_2N(CH_3)_2$	0.09 ± 0.12	0.29
67	—$COCH_3$	1.70 ± 0.05	1.56
68	—COC_3H_7 (*n*)	1.59 ± 0.09	1.56
69	—COC_4H_g (*n*)	1.45 ± 0.12	1.56
70	—CH_2COCH_3	0.69 ± 0.17	0.69
71	—CH_2COH	0.69 ± 0.17	0.69
72	—C_2H_4COH	0.15 ± 0.12	0.32
73	—$C_2H_4COCH_3$	0.11 ± 0.12	0.32
74	—$COOCH_3$	1.94 ± 0.07	2.05
75	—$COOC_2H_5$	1.89 ± 0.07	2.05
76	—$COOC_3H_7$ (*n*)	1.99 ± 0.12	2.05
77	—$COOC_3H_7$ (*i*)	1.91 ± 0.07	2.05
78	—CH_2COOH	1.08 ± 0.17	1.23
79	—CH_2COOCH_3	1.09 ± 0.07	1.23
80	—C_2H_4COOH	0.34 ± 0.17	0.53
81	—$C_2H_4COOCH_3$	0.30 ± 0.07	0.53
82	—$C_2H_4COOC_2H_5$	0.22 ± 0.19	0.53
83	—NO_2	4.73 ± 0.17	4.72
84	—CH_2NO_2	1.37 ± 0.17	1.59
85	—$CHCH_3NO_2$	1.30 ± 0.17	1.59
86	—$CHC_2H_5NO_2$	1.30 ± 0.17	1.59
87	—$CH(NO_2)_2$	3.03 ± 0.17	3.18
88	—$C(NO_2)_3$	4.62 ± 0.17	4.77
89	—$C_2H_4NO_2$	0.47 ± 0.17	0.73
90	—$C_3H_6NO_2$	0.48 ± 0.17	0.42
91	—CN	3.48 ± 0.07	3.37
92	—CH_2CN	1.15 ± 0.17	1.67
93	—C_2H_4CN	0.87 ± 0.07	0.78
94	—C_3H_6CN	0.43 ± 0.07	0.50
95	—$C{\equiv}CH$	1.75 ± 0.07	1.72
96	—$C{\equiv}CCH_3$	1.81 ± 0.07	1.79
97	—$CH_2C{\equiv}CH$	0.76 ± 0.17	0.82
98	—$C_2H_4C{\equiv}CH$	0.19 ± 0.07	0.31
99	—$C_3H_6C{\equiv}CH$	0.17 ± 0.07	0.19
100	—$SOCH_3$	2.89 ± 0.17	2.87
101	—CH_2SOCH_3	1.30 ± 0.17	1.18
102	—SO_2CH_3	3.72 ± 0.17	3.65
103	—$SO_2C_3H_7$ (*i*)	3.59 ± 0.17	3.65
104	—$CH_2SO_2CH_3$	1.26 ± 0.17	1.63
105	—NCH_3NO_2	2.40 ± 0.07	2.27
106	—$NHCOCH_3$	1.59 ± 0.07	1.58
107	—$NHCOC_2H_5$	1.59 ± 0.07	1.58
108	—NCS	2.61 ± 0.17	2.67
109	—CH_2NCS	0.94 ± 0.17	0.74
110	—NCO	2.25 ± 0.17	2.30
111	—CH_2NCO	0.81 ± 0.17	0.66
112	—OCH_2Cl	2.58 ± 0.17	2.63
113	—$OCHCl_2$	3.08 ± 0.17	3.28
114	—OCH_2F	2.33 ± 0.17	2.18
115	—$OCHF_2$	2.83 ± 0.17	2.71
116	—$OCHO$	3.00 ± 0.17	2.83
117	—$OCH{\equiv}CH$	2.67 ± 0.12	2.59
118	—ONO_2	3.76 ± 0.07	3.68
119	—$COBr$	2.47 ± 0.17	2.58
120	—COF	2.46 ± 0.17	2.56
121	—$NHCOCH_3$	1.59	1.47
122	—$OCOCH_3$	2.33 ± 0.20	2.25
123	—CH_2OCOCH_3	0.79 ± 0.07	0.74
124	—$CONH_2$	1.75 ± 0.17	1.81
125	—CH_2ONO_2	1.49 ± 0.07	1.62
126	—$COCN$	3.43 ± 0.17	3.23

Table 1 continued.

No.	Substituent	σ^*	$\sigma_{\text{theor.}}^*$
127	—$CH{=}CHCl$ (*trans*)	0.96 ± 0.07	0.87
128	—$CH{=}CHCl$ (*cis*)	1.02 ± 0.07	1.20
129	—$CF{=}CH_2$	1.57 ± 0.17	1.42
130	—$CH{=}CHNO_2$ (*trans*)	1.76 ± 0.12	1.55
131	—$CH_2NHCONH_2$	0.39 ± 0.17	0.64
132		0.18 ± 0.07	0.22
133		0.27 ± 0.07	0.42
134	—$COCH{=}CH_2$	1.90 ± 0.17	1.76

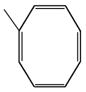
No.	Substituent	σ^*	$\sigma_{\text{theor.}}^*$
135	—$COC\equiv CH$	2.08 ± 0.07	2.28
136	—$CH{=}CHCOOH$	1.00 ± 0.07	0.99
137	—$CH_2NHCOCH_3$	0.45 ± 0.17	0.65
138	—$C_2H_4CONH_2$	0.18 ± 0.07	0.44
139	—$CH{=}C(CN)_2$	2.58 ± 0.07	2.64
140	—$CH{=}CHCH_2OOH$	0.69 ± 0.07	0.65
141	—$CH{=}CHCOOCH_3$	1.12 ± 0.07	1.12
142	—$C_2H_4CONHCH_3$	0.25 ± 0.07	0.44
143	—$SC(S)CH_3$	2.80 ± 0.17	2.61
144	—$SC(S)SC_2H_5$	2.86 ± 0.17	2.85
145	—$SC(S)OC_2H_5$	2.60 ± 0.17	2.69
146		1.00 ± 0.12	0.91

Table 2. Experimental and theoretical [calculated with Eqn (2)] inductive Taft's σ^* constants of aromatic substituents

No.	Substituent	σ^*	$\sigma_{\text{theor.}}^*$
147	—C_6H_5	0.75 ± 0.17	0.64
148	—C_6H_4F (*m*)	0.95 ± 0.17	0.87
149	—C_6H_4F (*p*)	0.81 ± 0.17	0.81
150	—C_6H_4Cl (*m*)	0.98 ± 0.17	0.90
151	—C_6H_4Cl (*p*)	0.87 ± 0.17	0.84
152	—C_6H_4I (*m*)	0.90 ± 0.17	0.94
153	—C_6H_4I (*p*)	0.87 ± 0.17	0.86
154	—C_6H_4Br (*p*)	0.86 ± 0.17	0.86
155	—$C_6H_4CH_3$ (*p*)	0.59 ± 0.17	0.64
156	—$C_6H_4OCH_3$ (*m*)	0.50 ± 0.17	0.76
157	—$C_6H_4OCH_3$ (*p*)	0.60 ± 0.17	0.74
158	—$C_6H_4C_2H_5$ (*p*)	0.59 ± 0.17	0.64
159	—$CH_2C_6H_5$	0.26 ± 0.17	0.21
160	—$CHCH_3C_6H_5$	0.36 ± 0.17	0.21
161	—$C_2H_4C_6H_5$	0.07 ± 0.17	0.09
162	—$CH_2C_6H_4CN$ (*p*)	0.41 ± 0.17	0.37
163	—C_6H_4 (*t*) C_4H_9	0.52 ± 0.17	0.64
164	—$C_6H_4(NO_2)_22,4$	1.89 ± 0.17	2.06
165	—$C_6H_4(NO_2)_23,5$	1.38 ± 0.17	1.39
166	—$C_6H_4NO_2$ (*m*)	1.22 ± 0.17	1.02
167	—$C_6H_4NO_2$ (*p*)	1.27 ± 0.17	0.92
168	—$C_6H_4NHCH_3$ (*p*)	0.55 ± 0.07	0.69
169	—C_6H_4NCS (*m*)	1.04 ± 0.07	0.83
170	—C_6H_4NCS (*p*)	0.95 ± 0.07	0.78
171	—$C_6H_4N(CH_3)_2$ (*m*)	0.61 ± 0.07	0.71
172	—$C_6H_4N(CH_3)_2$ (*p*)	0.43 ± 0.07	0.69
173	—$C_6H_4NH_2$ (*m*)	0.61 ± 0.07	0.71
174	—$C_6H_4NH_2$ (*p*)	0.49 ± 0.07	0.67
175	—$C_6H_4N_3$ (*m*)	0.88 ± 0.07	0.81
176	—$C_6H_4ICl_2$ (*m*)	1.50 ± 0.02	1.25
177	—$C_6H_4ICl_2$ (*p*)	1.50 ± 0.02	1.18
178	—$C_6H_4IF_2$ (*m*)	1.30 ± 0.02	1.19
179	—$C_6H_4IF_2$ (*p*)	1.31 ± 0.02	1.12
180	—$C_6H_4IO_2$ (*m*)	1.13 ± 0.02	1.19
181	—$C_6H_4IO_2$ (*p*)	1.18 ± 0.02	1.17
182	—C_6H_4NHCN (*m*)	0.85 ± 0.02	0.87
183	—C_6H_4NHCN (*p*)	0.74 ± 0.02	0.85
184	—C_6H_4NHCOH (*m*)	0.83 ± 0.02	0.87
185	—C_6H_4NHCOH (*p*)	0.81 ± 0.02	0.84
186	—$NHCOC_6H_5$	1.68 ± 0.17	1.71
187	—$C_6H_4OCH_2Cl$ (*m*)	0.88 ± 0.17	1.05

No.	Substituent	σ^*	$\sigma_{\text{theor.}}^*$
188	—$C_6H_4OCH_2Cl$ (*p*)	0.76 ± 0.17	0.99
189	—$C_6H_4OCHCl_2$ (*m*)	0.90 ± 0.17	1.23
190	—$C_6H_4OCHCl_2$ (*p*)	0.96 ± 0.17	1.19
191	—$C_6H_4OCH_2F$ (*m*)	0.84 ± 0.17	1.00
192	—$C_6H_4OCH_2F$ (*p*)	0.71 ± 0.17	0.96
193	—OC_6H_5	2.47 ± 0.17	2.42
194	—OC_6H_4Cl (*m*)	2.58 ± 0.17	2.43
195	—OC_6H_4Cl (*p*)	2.63 ± 0.17	2.37
196	—OC_6H_4F (*m*)	2.52 ± 0.17	2.39
197	—OC_6H_4F (*p*)	2.45 ± 0.17	2.35
198	—OC_6H_4I (*m*)	2.45 ± 0.17	2.45
199	—OC_6H_4I (*p*)	2.40 ± 0.17	2.39
200	—$OC_6H_4NO_2$ (*m*)	2.77 ± 0.17	2.51
201	—$OC_6H_4CH_3$ (*m*)	2.34 ± 0.17	2.21
202	—$OC_6H_4CH_3$ (*p*)	2.31 ± 0.17	2.21
203	—$C_6H_4SC_2H_5$ (*p*)	0.74 ± 0.17	0.77
204	—$C_6H_4SCH_3$ (*m*)	0.79 ± 0.02	0.81
205	—$C_6H_4SCH_3$ (*p*)	0.73 ± 0.02	0.77
206	—SC_6H_4Cl (*m*)	2.03 ± 0.17	2.18
207	—SC_6H_4Cl (*p*)	1.98 ± 0.17	2.15
208	—SOC_6H_4Cl (*m*)	3.18 ± 0.17	3.24
209	—SOC_6H_4 Cl (*p*)	3.18 ± 0.17	3.24
210	—$SO_2C_6H_4Cl$ (*m*)	3.47 ± 0.17	3.83
211	—$SO_2C_6H_4Cl$ (*p*)	3.51 ± 0.17	3.84
212	—SC_6H_4F (*m*)	1.88 ± 0.17	2.14
213	—SC_6H_4F (*p*)	1.78 ± 0.17	2.12
214	—SOC_6H_4F (*m*)	3.17 ± 0.17	3.23
215	—SOC_6H_4F (*p*)	3.17 ± 0.17	3.22
216	—$SO_2C_6H_4F$ *m*)	3.55 ± 0.17	3.70
217	—$SO_2C_6H_4F$ (*p*)	3.45 ± 0.17	3.70
218	—$SC_6H_4NO_2$ (*m*)	2.04 ± 0.17	2.26
219	—$SC_6H_4NO_2$ (*p*)	2.34 ± 0.17	2.21
220	—$SOC_6H_4NO_2$ (*m*)	3.22 ± 0.17	3.32
221	—$SOC_6H_4NO_2$ (*p*)	3.26 ± 0.17	3.31
222	—SC_6H_5	1.89 ± 0.17	1.99
223	—SOC_6H_5	3.24 ± 0.17	3.09
224	—$SO_2C_6H_5$	3.27 ± 0.17	3.60
225	—SC_6H_4CN (*p*)	2.30 ± 0.17	2.17
226	—$SC_6H_4CH_3$ (*m*)	1.90 ± 0.17	1.99
227	—$SC_6H_4CH_3$ (*p*)	1.91 ± 0.17	1.99
228	—$SOC_6H_4CH_3$ (*m*)	3.01 ± 0.17	3.09

Table 2 continued.

No.	Substituent	σ^*	$\sigma_{\text{theor.}}^*$	No.	Substituent	σ^*	$\sigma_{\text{theor.}}^*$
229	—$SOC_6H_4CH_3$ (*p*)	3.03 ± 0.17	3.09	252	—$C_6H_4CH_2F$ (*p*)	0.77 ± 0.03	0.79
230	—$SC_6H_4OCH_3$ (*m*)	1.90 ± 0.17	2.09	253	—$C_6H_4CH_2NH_2$ (*m*)	0.66 ± 0.03	0.68
231	—$SC_6H_4OCH_3$ (*p*)	1.67 ± 0.17	2.07	254	—$C_6H_4CH_2NH_2$ (*p*)	0.61 ± 0.03	0.67
232	—$SOC_6H_4OCH_3$ (*p*)	3.02 ± 0.17	3.15	255	—$C_6H_4 + C{\equiv}CH$ (*p*)	0.81 ± 0.03	0.75
233	—$SO_2C_6H_4OCH_3$ (*m*)	3.26 ± 0.17	3.72	256	—$C_6H_4CH_2CN$ (*m*)	0.86 ± 0.03	0.83
234	—$SO_2C_6H_4OCH_3$ (*p*)	3.25 ± 0.17	3.72	257	—$C_6H_4CH_2CN$ (*p*)	0.83 ± 0.03	0.81
235	—$SC_6H_4SCH_3$ (*m*)	1.94 ± 0.17	2.12	258	—$C_6H_4CH{=}CH_2$ (*m*)	0.71 ± 0.03	0.68
236	—$SC_6H_4SCH_3$ (*p*)	1.70 ± 0.17	2.09	259	—$C_6H_4CH{=}CH_2$ (*p*)	0.69 ± 0.03	0.66
237	—C_6H_4CN (*m*)	1.13 ± 0.03	0.92	260	—$C_6H_4COCH_3$ (*m*)	0.93 ± 0.03	0.89
238	—C_6H_4CN (*p*)	1.21 ± 0.03	0.85	261	—$C_6H_4COCH_3$ (*p*)	1.04 ± 0.03	0.83
239	—$C_6H_4CHF_2$ (*m*)	0.93 ± 0.03	0.96	262	—$C_6H_4COOC_2H_5$ (*p*)	1.00 ± 0.03	0.90
240	—$C_6H_4CHF_2$ (*p*)	0.95 ± 0.03	0.94	263	—$C_6H_4COOCH_3$ (*m*)	0.95 ± 0.03	0.98
241	—$C_6H_4CHCl_2$ (*m*)	0.92 ± 0.03	1.02	264	—$C_6H_4COOCH_3$ (*p*)	1.03 ± 0.03	0.90
242	—$C_6H_4CHCl_2$ (*p*)	0.93 ± 0.03	0.96	265	—$C_6H_4C{\equiv}CCH_3$ (*p*)	0.74 ± 0.03	0.75
243	—$C_6H_4CHBr_2$ (*m*)	0.92 ± 0.03	1.07	266	—$C_6H_2C(CN_2)CH_3$ (*m*)	1.13 ± 0.03	1.02
244	—$C_6H_4CHBr_2$ (*p*)	0.93 ± 0.03	1.00	267	—$C_6H_2C(CN_2)CH_3$ (*p*)	1.11 ± 0.03	0.98
245	—$C_6H_4CHI_2$ (*m*)	0.89 ± 0.03	1.08	268	1-Naphthyl	0.77 ± 0.17	0.95
246	—$C_6H_4CHI_2$ (*p*)	0.89 ± 0.03	1.02	269	2-Naphthyl	0.74 ± 0.17	0.81
247	—C_6H_4COH (*m*)	0.99 ± 0.03	0.89	270	2-Furyl	1.02 ± 0.17	1.11
248	—C_6H_4COH (*p*)	1.03 ± 0.03	0.85	271	3-Furyl	0.61 ± 0.17	0.80
249	—C_6H_4COOH (*m*)	0.95 ± 0.02	0.81	272	2-Thienyl	1.32 ± 0.03	1.28
250	—C_6H_4COOH (*p*)	1.02 ± 0.02	0.90	273	3-Thienyl	0.61 ± 0.03	0.76
251	—$C_6H_4CH_2F$ (*m*)	0.78 ± 0.03	0.80				

Table 3. Experimental and theoretical [calculated with Eqn (2)] inductive Taft's σ^* constants of organoelement substituents

No.	Substituent	σ^*	$\sigma_{\text{theor.}}^*$	No.	Substituent	σ^*	$\sigma_{\text{theor.}}^*$
274	—$As(CH_3)_2$	0.78 ± 0.50	0.62	308	—SePh	1.55 ± 0.07	1.44
275	—$As(C_2H_5)_2$	0.52 ± 0.02	0.62	309	—$SeC_6H_4CH_3$ (*m*)	1.66 ± 0.17	1.44
276	—$As(C_2H_3)_2$	0.78 ± 0.50	0.84	310	—$SeC_6H_4CH_3$ (*p*)	1.84 ± 0.17	1.44
277	—$C_6H_4AsPh_2$ (m)	0.74 ± 0.02	0.76	311	—SeC_6H_4Br (*p*)	1.42 ± 0.17	1.60
278	—$C_6H_4AsPh_2$ (p)	0.78 ± 0.02	0.76	312	—SeC_6H_4Cl (*m*)	1.52 ± 0.17	1.57
279	—$AuP(OPh)_3$	4.71 ± .02	−4.87	313	—SeC_6H_4Cl (*p*)	1.46 ± 0.17	1.54
280	—$AuP(Ph)_3$	−5.10 ± .02	−5.23	314	—$SeC_6H_4NO_2$ (*m*)	1.66 ± 0.17	1.68
281	—$AuP(CH_3)_3$	−5.65 ± .02	−5.45	315	—$SeC_6H_4NO_2$ (*p*)	1.84 ± 0.17	1.58
282	—$AuP(PhCH_3)_3$	−5.30 ± .02	−5.38	316	—$SeC_6H_4SCH_3$ (*p*)	1.24 ± 0.17	1.52
283	—$Ga(CH_3)_2$	−1.31 ± .02	−1.19	317	—$SeC_6H_4OC_2H_5$ (*p*)	1.19 ± 0.17	1.50
284	—$Ga(C_2H_3)_2$	−0.89 ± .02	−0.99	318	—$SnBr_3$	2.06 ± 0.08	1.77
285	—$Ge(CH_3)_3$	−0.04 ± .08	−0.14	319	—$SnCl_2CH_3$	0.90 ± 0.08	1.08
286	—$Ge(C_2H_5)_3$	−0.04 ± .08	−0.14	320	—$SnCl(CH_3)_2$	0.28 ± 0.08	0.30
287	—$Ge(Ph)_3$	0.28 ± 0.08	0.32	321	—$Sn(CH_3)_3$	−0.04 ± 0.08	−0.30
288	—$C_6H_4GeBr_3$ (*p*)	1.22 ± 0.02	1.37	322	—$SnCl_2Ph$	0.98 ± 0.08	1.17
289	—$C_6H_4GeCl_3$ (*p*)	1.27 ± 0.02	1.26	323	—$Sn(C_2H_3)_3$	−0.26 ± .08	−0.14
290	—$C_6H_4GeF_3$ (*p*)	1.39 ± 0.02	1.11	324	—$SiBr_3$	2.39 ± 0.17	2.33
291	—HgBr	0.05 ± 0.08	0.06	325	—$SiCl_2CH_3$	1.46 ± 0.13	1.40
292	—HgC_2H_3	−0.50 ± .08	−0.41	326	—$SiCl(CH_3)_2$	0.65 ± 0.17	0.64
293	—$HgOCOCH_3$	−0.12 ± .08	−0.06	327	—$SiF(CH_3)_2$	0.45 ± 0.17	0.55
294	—$C_6H_4HgCH_3$ (*m*)	1.00 ± 0.03	0.60	328	—$SiH(CH_3)_2$	−0.16 ± .17	−0.12
295	—$C_6H_4HgCH_3$ (*p*)	0.77 ± 0.03	0.60	329	—$SiCl_3$	2.41 ± 0.17	2.16
296	—C_6H_4HgCN (*m*)	0.90 ± 0.03	0.72	330	—$C_6H_4SiBr_3$ (*m*)	1.04 ± 0.03	1.20
297	—C_6H_4HgCN (*p*)	0.94 ± 0.03	0.70	331	—$C_6H_4SiBr_3$ (*p*)	1.11 ± 0.03	1.06
298	—C_6H_4HgCl (*m*)	0.94 ± 0.03	0.70	332	—$C_6H_4SiCl_3$ (*m*)	1.04 ± 0.03	1.16
299	—C_6H_4HgCl (*p*)	0.95 ± 0.03	0.69	333	—$C_6H_4SiCl_3$ (*p*)	1.10 ± 0.03	1.12
300	—C_6H_4HgF (*m*)	0.94 ± 0.03	0.68	334	—$C_6H_4SiF_3$ (*m*)	1.09 ± 0.03	1.09
301	—C_6H_4HgF (*p*)	0.94 ± 0.03	0.68	335	—$C_6H_4SiF_3$ (*p*)	1.17 ± 0.03	1.07
302	—Li	−2.89 ± .50	−2.65	336	—$C_6H_4SiH_3$ (*m*)	0.74 ± 0.03	0.63
303	—OLi	0.87 ± 0.50	0.80	337	—$C_6H_4SiH_3$ (*p*)	0.77 ± 0.03	0.63
304	—MgBr	−3.11 ± 0.5	−3.11	338	—$C_6H_4SiCl_2Me$ (*m*)	0.92 ± 0.03	0.98
305	—MgCl	−3.16 ± 0.5	−3.16	339	—$C_6H_4SiCl_2Me$ (*p*)	0.98 ± 0.03	0.94
306	—$SeCH_3$	0.94 ± 0.17	1.28	340	—$C_6H_4SiClMe_2$ (*m*)	0.82 ± 0.03	0.81
307	—SeH	1.29 ± 0.13	1.28	341	—$C_6H_4SiClMe_2$ (*p*)	0.85 ± 0.03	0.79

Table 3 continued.

No.	Substituent	σ^*	$\sigma_{theor.}^*$
342	—$C_6H_4SiMe_2F$ (*m*)	0.79 ± 0.03	0.79
343	—$C_6H_4SiMe_2F$ (*p*)	0.84 ± 0.03	0.77
344	—$C_6H_4SiHMe_2$ (*m*)	0.71 ± 0.03	0.63
345	—$C_6H_4SiHMe_2$ (*p*)	0.73 ± 0.03	0.63
346	—$C_6H_4SiMe_3$ (*m*)	0.64 ± 0.03	0.63
347	—$C_6H_4SiMe_3$ (*p*)	0.65 ± 0.03	0.63
348	—$C_6H_4Si(NMe_2)_3$ (*m*)	0.67 ± 0.03	0.74
349	—$C_6H_4Si(NMe_2)_3$ (*p*)	0.67 ± 0.03	0.71
350	—$C_6H_4SiMe_2Ph$ (*m*)	0.73 ± 0.03	0.67
351	—$C_6H_4SiMe_2Ph$ (*p*)	0.75 ± 0.03	0.65
352	—$C_6H_4SiMePh_2$ (*m*)	0.75 ± 0.03	0.69
353	—$C_6H_4SiMePh_2$ (*p*)	0.77 ± 0.03	0.68
354	—$C_6H_4SiPh_3$ (*m*)	0.82 ± 0.03	0.74
355	—$C_6H_4SiPh_3$ (*p*)	0.83 ± 0.03	0.72
356	—PBr_2	1.73 ± 0.17	2.12
357	—$P(CH_3)_2$	0.55 ± 0.17	0.34
358	—$P(C_2H_3)_2$	0.55 ± 0.17	0.57
359	—PCl_2	1.73 ± 0.17	2.05
360	—PF_2	2.38 ± 0.17	2.17
361	—PH_2	0.17 ± 0.17	0.34
362	—$PO(CH_3)_2$	1.39 ± 0.07	1.42
363	—$PO(OCH_3)_2$	2.21 ± 0.07	2.28
364	—$PO(C_2H_5)_2$	1.68 ± 0.07	1.42
365	—P(O)MeOEt	1.82 ± 0.07	1.85
366	—$PO(nC_3H_7)_2$	1.55 ± 0.07	1.42
367	—$PO(nC_4Hg)_2$	1.48 ± 0.07	1.42
368	—P(O)BuOBu	1.62 ± 0.07	1.85
369	—$PO(O\text{-}nBu)_2$	1.78 ± 0.07	2.28
370	—$CH_2PO(CH_3)_2$	0.68 ± 0.07	0.55
371	—$CH_2P(OCH_3)_2$	0.80 ± 0.07	1.21
372	—$CH_2P(O)MeOEt$	0.70 ± 0.07	0.88
373	—$CH_2PO(C_2H_5)_2$	0.62 ± 0.07	0.55
374	—$CH_2P(O)EtOEt$	0.67 ± 0.07	0.88
375	—$CH_2P(O)Pr_2$	0.59 ± 0.07	0.55
376	—$C_6H_4PMe_2$ (*m*)	0.73 ± 0.03	0.67
377	—$C_6H_4PMe_2$ (*p*)	0.72 ± 0.03	0.66
378	—$C_6H_4P(O)Me_2$ (*m*)	1.01 ± 0.03	0.90
379	—$C_6H_4P(O)Me_2$ (*p*)	1.06 ± 0.03	0.84
380	—$C_6H_4P(OMe)_2$ (*m*)	0.79 ± 0.03	0.86
381	—$C_6H_4P(OMe)_2$ (*p*)	0.81 ± 0.03	0.81
382	—$C_6H_4PO(OMe)_2$ (*m*)	0.95 ± 0.03	1.03
383	—$C_6H_4PO(OMe)_2$ (*p*)	1.01 ± 0.03	0.98
384	—$C_6H_4PO(OEt)_2$ (*m*)	0.92 ± 0.03	1.03
385	—$C_6H_4PO(OEt)_2$ (*p*)	0.97 ± 0.03	0.98
386	—$C_6H_4P(O)Ph_2$ (*m*)	1.02 ± 0.03	0.98
387	—$C_6H_4P(O)Ph_2$ (*p*)	1.07 ± 0.03	0.94
388	—$C_6H_4PCl_3$ (*m*)	1.08 ± 0.03	1.09
389	—$C_6H_4PCl_3$ (*p*)	1.14 ± 0.03	0.98
390	—$C_6H_4P(O)Cl_2$ (*m*)	1.26 ± 0.03	1.32
391	—$C_6H_4P(O)Cl_2$ (*p*)	1.34 ± 0.03	1.16
392	—$C_6H_4PF_2$ (*m*)	1.05 ± 0.03	1.01
393	—$C_6H_4PF_2$ (*p*)	1.13 ± 0.03	0.95
394	—$C_6H_4PH_2$ (*m*)	0.74 ± 0.03	0.67
395	—$C_6H_4PH_2$ (*p*)	0.73 ± 0.03	0.66
396	—$C_6H_4PO(OH)_2$ (*m*)	0.96 ± 0.03	1.03
397	—$C_6H_4PO(OH)_2$ (*p*)	1.00 ± 0.03	0.98

substituent from other inductive scales taken from Ref. 7. The recalculation was based on preliminarily obtained correlation dependences, only those having correlation coefficients of not less than 0.98 being included. By recalculating from different independent scales for the same substituent, we obtained several Taft inductive constants (commonly five or six), which were then averaged. Thus, we constructed a unified basic scale of the Taft inductive constants σ^* for a total of 427 substituents,[5] which are presented in Tables 1–4.

3. As follows from point 1, the atomic level of additivity is accepted. The inductive effect of a substituent is produced by the combined inductive actions of the constituent atoms: these in turn must each be proportional to the inductive ability of an atom (σ_A) and inversely proportional to some function of the distance of this atom from the reaction center. Since the type of

Table 4. Experimental and theoretical [calculated with Eqn (2)] inductive Taft's σ^* constants of charged substituents

No.	Substituent	σ^*	$\sigma_{theor.}^*$
398	—COO^-	−1.08 ± .17	−1.08
399	—CH_2COO^-	−0.07 ± .17	−0.39
400	—$CH{=}CHCOO^-$	−0.03 ± .17	0.01
401	—C^-HCN	1.60 ± 0.07	1.70
402	—$C^-HCOOC_2H_5$	1.25 ± 0.07	1.15
403	—SO_3^-	0.89 ± 0.17	0.68
404	—$CH_2SO_3^-$	−0.09 ± .17	0.32
405	—$S^+(CH_3)_2$	5.76 ± 0.07	5.85
406	—$C_2H_4S^+(CH_3)_2$	1.60 ± 0.07	1.12
407	—$C_3H_6S^+MeEt$	0.73 ± 0.07	0.68
408	—$C_4H_8S^+MeEt$	0.38 ± 0.07	0.43
409	—P^+Me_3	2.51 ± 0.17	2.67
410	—P^+Et_3	1.86 ± 0.17	2.67
411	—P^+EtMe_2	3.66 ± 0.17	2.67
412	—$PhCOO^-$ (*m*)	0.60 ± 0.03	0.58
413	—$PhCOO^-$ (*p*)	0.55 ± 0.03	0.56
414	—$NH_2^+Me_2Cl$	3.75 ± 0.17	4.01
415	—$NH_2^+Me\ Cl^-$	3.69 ± 0.17	4.01
416	—NH_2^+Me	3.76 ± 0.17	4.01
417	—NH^+Me_2	4.38 ± 0.17	4.01
418	—NH_2^+Et	3.75 ± 0.17	4.01
419	—$N^+Me_3Cl^-$	4.48 ± 0.17	4.01
420	—NH_2^+Pr (*n*)	3.75 ± 0.17	4.01
421	—N^+Me_3	4.38 ± 0.17	4.01
422	—NH_2^+Bu (*n*)	3.75 ± 0.17	4.01
423	—NH_2^+Bu (*i*)	3.75 ± 0.17	4.01
424	—NH_3^+	3.78 ± 0.17	4.01
425	—$CH_2N^+HMe_2$	1.08 ± 0.17	1.48
426	—$CH_2N^+Me_3$	1.02 ± 0.17	1.48

Table 5. Empirical atomic σ_A and group σ_G constants obtained from experimental Taft constants

Atom	σ_A	Atom	σ_A	Group	σ_G
—F	5.88 ± 0.29	—P<	1.23 ± 0.32	—C=C—	0.94 ± 0.15
—Cl	7.62 ± 0.64			>C=O	3.29 ± 0.24
—Br	8.91 ± 0.73	>P=	1.50 ± 0.23	—COOR	4.48 ± 0.14
				—NO$_2$	10.23 ± 0.29
—I	9.71 ± 1.24	>P$^+$<	9.60 ± 3.22	—CN	7.56 ± 0.45
—O—	3.25 ± 0.06			—C≡C—	3.86 ± 0.08
O=	7.52 ± 0.70				
—O$^-$	−4.84 ± 2.10	—Sn<	−1.23 ± 0.50	>S=0	8.69 ± 0.55
—S—	5.03 ± 0.12	>As—	2.38 ± 0.08	>SO$_2$	11.14 ± 0.46
S=	17.14 ± 1.72			>C=S	8.24 ± 0.19
>S=	4.91 ± 0.62	>As$^+$<	6.80[a]	—NCS	5.24 ± 0.48
>S⫽	3.28 ± 0.70	>B—	−0.09[a]	—NCO	4.51 ± 0.42
				—NC	6.72[a]
>S$^+$	19.60 ± 0.93	—Ga<	−4.62 ± 0.30	—NO	3.55[a]
—S$^-$	−0.14[a]			—N$_3$	4.51[a]
=S—	−8.37 ± 1.06	—Hg—	−2.00 ± 0.12	—SCN	10.6[a]
		—Li	−10.6 ± 0.80	>N→O	7.17[a]
—N<	1.78 ± 0.16	—Mg—	−14.3 ± 0.04	>P=O	4.38 ± 0.21
N≡	11.06 ± 1.54			>P=S	2.52 ± 0.16
—N⫽	4.89 ± 0.77	>Pb<	2.42[a]	—Ph	1.45 ± 0.12
				—OPh	4.45 ± 0.14
>N$^+$<	8.56 ± 0.34	—Sb<	1.44[a]	—SPh	6.44 ± 0.25
				—SOPh	9.98 ± 0.28
>C<	0.00	>Ge<	−0.52 ± 0.40	—SO$_2$Ph	11.43 ± 0.32
				1—Naphthyl	2.17 ± 0.10
>C=	0.70 ± 0.14	>Si<	−0.40 ± 0.26	2—Naphthyl	1.84 ± 0.09
—C≡	2.90 ± 0.58			—AuAs<	−27.9 ± 0.6
C$_{ar.}$	1.25 ± 0.10	—Se—	4.68 ± 0.98	—AuP<	−27.7 ± 0.5
		—H	0.00	—CO$_2^-$	−2.11 ± 0.73
>C$^-$	0.90 ± 0.22			—SO$_3^-$	2.14 ± 1.32

[a] Constants were calculated from unit σ^* values.

this dependence is determined by the mechanism of transmission of the inductive effect, which still remains uncertain, we studied as possible candidate exponential functions of various parameters characterizing the remoteness from the reaction center, r^m, n^m, l^m (where r is the distance between an atom and the reaction center in three-dimensional coordinates, n is the number of bonds between the atom and the reaction center and l is the sum of the distances of these bonds), and also their possible superpositions. The exponents m were varied from 1 to 3. Thus, the solution was sought in the form[4]

$$\sigma^* = \sum_{i=1}^{n} \frac{(\sigma_A)_i}{S_i} \qquad (1)$$

where S_i is one of the above-mentioned functions of remoteness of atoms from the reactive center.

4. The inductive effect of alkyl groups is taken to be identical with zero, which substantially simplifies the problem since, clearly, σ_A(H) and σ_A(C) are zero in this case. For this assumption to be as justified as possible, a saturated carbon atom was chosen as the reaction center. This choice is also of importance for the subsequent calculation of the spatial atomic coordinates of a substituent.

It is within the framework of the above postulates that the final solution was sought on a computer. Such an approach seems to be more logical, since it enables one first to reveal formally the existence or absence of a solution to equations like such as Eqn (1) (i.e. to check whether for the chosen degree of additivity there exists a measure of the inductive effect, σ_A, that is constant for a given atom in a given valence state) and only then to analyze the physical meaning of this measure.

Without going into details of the investigation performed, we should mention that the approach we chose proved to be fairly efficient, the σ^* constants being best modeled by the square of the distance to the reaction center:[4]

$$\sigma^* = \sum_{i=1}^{n} \frac{(\sigma_A)_i}{r_i^2} \qquad (2)$$

where σ^* is the inductive constant of a substituent on the Taft scale, n is the number of atoms in the substituent, $(\sigma_A)_i$ is the inductive power of the i th atom, which depends on the chemical nature of the element and its valence state, determined from Eqn (2) using a least-squares procedure (empirical σ_A values for various elements are listed in Table 5), and r_i is the distance from this atom to the reaction center (four-coordinate carbon).

The r_i values were calculated from bond distances and valence and torsional angles on three-dimensional Cartesian coordinates, when possible taking account of the actual molecular conformation taken from Ref. 8. In the case when the conformation was indeterminate, we solved an inverse mathematical problem: theoretical values of σ^* were calculated for any possible conformation of a substituent and, judging from the closeness to the experimental value for this substituent, its actual structure was determined, just as we have done previously in terms of the model of the frontier steric effect.[123] The relationship between the inductive effect of a substituent and its conformation will be considered in more detail below.

The proposed additive approach describes with a high degree of accuracy the inductive constants of a variety of substituents for nearly the whole available body of σ^* constants. Table 1 lists the experimental and theoretical [calculated by Eqn (2)] σ^* constants for 146 of the most widely occurring organic non-aromatic substituents. These values show a perfect correlation with a zero constant term and unit slope, in full agreement with the mathematical expectation for these parameters:[4]

$$\sigma^*_{\mathrm{theor.}} = -(0.078 \pm 0.022) + (1.029 \pm 0.012)\sigma^*_{\mathrm{exp.}}$$
$$N = 146, r = 0.9889, S_0 = 0.1480. \qquad (3)$$

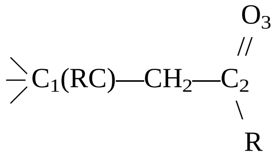
Similarly excellent linear correlations with a correlation coefficient of not less than 0.98 are observed between $\sigma^*_{\mathrm{theor.}}$ and the inductive constants for all the 25 reference series used by us to form a basic experimental scale for inductive Taft constants.

The high degree of additivity of the proposed model enabled us not only to determine the inductive substituent effect from the atomic constants σ_A, but also to use in calculations, for the sake of convenience, the group values σ_G obtained in terms of Eqn (2) for functional groups of the types C=O, COOR, CN and NO_2 that occur most widely in organic chemistry (here the distance from the reactive center to the nearest atom of the functional group is taken as r). The σ_G constants for the most frequently considered groups are also listed in Table 5.

Generally, the use of these has no detrimental effect on the accuracy of calculating inductive constants, which confirms a certain integrity and high degree of additivity of the proposed approach.

The reproducibility of various calculation techniques in the framework of the model under discussion will be illustrated by the example of the alkylcarbonylmethyl group.

The calculated distances from the reactive center to the C^1 atom are $r_{1-2} = 2.31$. $r_{1-3} = 3.66$ Å .



In view of the assumption that alkyl fragments should exhibit no inductive properties, i.e. $\sigma_G(\mathrm{R}) = 0$ and $\sigma_G(\mathrm{CH_2}) = 0$, the inductive constant σ^* of the carbonyl group can be calculated by two different methods:

(a) by directly using the group constant $\sigma_G(\mathrm{COR})$:

$$\sigma^*(\mathrm{COR}) = \sigma_G(\mathrm{COR})/r^2_{1-2} = 0.62$$

(b) starting from the σ_A, constants of atoms that constitute the substituent:

$$\sigma^*(\mathrm{COR}) = \sigma_A(=\mathrm{C}<)/r^2_{1-2} + \sigma_A(\mathrm{O}=)/r^2_{1-3} = 0.69$$

The corresponding experimental σ^* constants of the given substituent have an average value of 0.69 within the basis scale (Tables 1–4).

In view of the fact that inductive constants are usually experimentally determined to an accuracy of ±15%. We can say with confidence that the σ^* constant, calculated by us for the above-mentioned substituent using various methods, agree well with the experimental data.

Hence the proposed approach can make use of any degree of additivity (atomic, group or superposition of these) to give fairly acceptable results.

At the same time, it is evident that the use of group parameters σ_G substantially simplifies the calculation procedure, therefore being more convenient in actual practice. Their employment is particularly appropriate in the case of symmetric conformationally homogeneous substituents such as NO_2 and CN, which always behave as a single molecular fragment and rarely suffer any chemical transformations. Moreover, in some, although rare cases, the actual electronic structure of a functional group can hardly be modeled by any single canonical structure; then it is more appropriate and correct to use the total group constant of a given molecular fragment as a whole.

Electronic effect of aromatic substituents

In considering inductive interactions for the aromatic series it is necessary to take into account conjugation between the reaction center and the substituent. Extensive studies in this field resulted in the appearance of two- and three-parameter equations, implying separation of the electron effect into inductive and resonance components.[9]

Thus far, a fairly large number of different methods have been developed for selecting inductive constants that would be free from direct polar conjugation. All these are based on solving two- or three-parameter equations (approaches of Taft. Exner, Pal'm. Yukawa-Tsuno, Swain–Lupton. etc.) and involve certain theoretical assumptions that are often subject to severe criticism. The main problem of such approaches is whether the obtained inductive and resonance components are indeed mutually independent, which cannot be guaranteed by any of the existing methods. Obviously, almost all of them are based on the reactivities of substituted benzoic acids for which conjugation between the aryl and carboxy groups is possible. Hence constants that are 'free from direct polar conjugation' are only conditionally inductive.

However, the very existence of various multiparameter relations indicates that the nature of the inductive effects in the aliphatic and aromatic series is the same and the effects can be compared quantitatively.[9]

We made an attempt to calculate the inductive constants of aromatic substituents in terms of our model, which allows the evaluation of their purely inductive influence on the reaction center, without any contribution from the resonance component.

On the basis of available published data, we constructed a unified scale of averaged inductive constants for a number of aromatic substituents in a manner similar to that reported.[10] Using separately derived correlation equations, we recalculated the 'zero' inductive constants $\sigma_m{}^0$ and $\sigma_p{}^0$ (which represent the inductive influence of an aryl radical with a substituent in *meta* and *para* positions, respectively) and also the σ constants for aromatic substituents, taken from various scales.[7] to the averaged basis scale of the Taft σ* constants (Table 2).

On the basis of the principle of additivity of the group influence of a substituent on the reaction center, which underlies our model, and the previously described procedure,[4] we calculated the group constant σ_G for the phenyl radical and the σ_A value for the aromatic carbon atom (Table 5), using Eqns. (4) and (5), respectively:[10]

$$\sigma^*(\mathrm{Ph}) = \sigma_G(\mathrm{Ph})/r^2 \tag{4}$$

$$\sigma^*(\mathrm{Ph}) = \sigma_A(\mathrm{C_{arom.}})(1/r_1^2 + 1/2r_2^2 + 1/2r_3^2 + 1/r_4^2) \tag{5}$$

Here, σ_G(Ph) is the inductive ability of the phenyl fragment on the reaction center, $\sigma_A(\mathrm{C_{arom.}})$ is the inductive ability of the aromatic carbon atom, r_1, r_2, r_3 and r_4 are the distances from the reaction center to the *ipso*-, *ortho*-, *meta*- and *para*-carbon atoms, respectively, and σ*(Ph) are the inductive constants for substituents containing a phenyl or *meta*- or *para*-alkylphenyl fragments at various distances from the reaction center.

In this case the σ_A constant of the aromatic carbon atom was 1.25 ± 0.10, which is fairly close to the σ_A constant of an sp^2-hybridized carbon atom (0.70). However, the fact that this constant is higher, thus approaching the corresponding value for an sp-hybridized carbon atom [$\sigma_A(\mathrm{C_{sp}}) = 2.90$], once again confirms the dependence of σ_A constants on the valence state of atoms, indicating a higher electronegativity of aromatic carbons as compared with the conventional sp^2 state. The latter is, in turn, in good agreement with the classical concepts of aromatic conjugation.

Further, using σ_A constants obtained earlier in calculating inductive constants of organic substituents, we evaluated the inductive effect *per se* for aromatic substituents functionalized in *meta* and *para* positions, including aromatic heterocyclicrings. We did not evaluate the inductive influence of *ortho*-substituted fragments, since it is reasonably safe to suggest that steric interactions contribute to the corresponding experimental σ* constants.[10]

Using the procedure describing above, we calculated inductive effects for more than 100 aromatic substituents (Table 2). The calculated constants correlate well with the corresponding experimental values:

Aromatic substituents:

$$\sigma^*_{\mathrm{theor.}} = (0.046 \pm 0.025) + (0.944 \pm 0.014)\sigma^*_{\mathrm{exp.}}$$
$$N = 127, r = 0.9854, S_0 = 0.156 \tag{6}$$

Equation (6), having a zero constant term and a nearly unit slope, almost coincides with that obtained earlier for non-aromatic organic substituents.

It should also be noted that to simplify the calculqation procedure, total group constants of of various aromatic fragments (Table 4) can be conveniently used instead of σ_A values of aromatic carbons. This simplification has virtually no detrimental effect on the accuracy of the results obtained.

Thus, the inductive constants of aromatic substituents calculated in terms of the present approach reproduce fairly adequately the corresponding experimental values. The deviations of the theoretical constants from the experimental values are presumably due to the presence in the latter of a mesomeric component, especially since it is the substituents that exhibit a tendency for mesomeric interaction (NO_2, CN, OR, NR_2) which show the largest deviations from the linear dependence in Eqn (6). In this case, it can be readily seen that substituents exhibiting a donor or acceptor mesomeric effect deviate in opposite directions, being correspondingly underrated or overrated with respect to the experimental constant.

Since the proposed model describes only the inductive effect of a substituent, taking no account of the contribution from conjugation, it is obvious that the resulting values can be used for, among other things, to separate adequately the inductive and mesomeric components in evaluating the reactivity of aromatic compounds. Indeed, a correlation between the deviations from Eqn (6) and the resonance constants of the corresponding substituents is observed for a wide variety of substituents exhibiting the strongest tendency for mesomeric interaction.

Thus, our investigation has shown that the model of the inductive effect proposed by us, on the whole, describes fairly adequately inductive constants of a variety of aromatic substituents, making it possible to analyze, when necessary, also finer aspects related to aromatic conjugation and mesomeric or conformational effects.

Inductive Effect of organoelement substituents

We increased the number of subjects to be studied by extending the proposed approach to organoelement substituents that have not been considered previously.[11] (Note that a large group of organoelement substituents, incorporating such atoms as O, S and N, have already been included in the previous substituent sets).

In the case of organoelement substituents, too, the nature of the earlier established relations remained unchanged and including new points only improved the corresponding correlations.

Thus, theoretical inductive constants calculated in the present work for more than 100 organoelement substituents (Table 3) form with the corresponding experimental values taken from Ref. 7 an excellent linear correlation with a zero constant term and a nearly unit slope:

$$\sigma^{*}_{\mathrm{theor.}} = (0.023 \pm 0.015) + (0.994 \pm 0.010)\sigma^{*}_{\mathrm{exp.}}$$
$$N = 124, r = 0.9930, S_0 = 0.1616 \qquad (7)$$

Relation (7) is in nearly complete agreement with similar relations established earlier for organic and aromatic substituents [Eqns (3) and (6) and Refs 4 and 10.

Inductive effect of charged groups

We also extended the proposed approach to the inductive effect of substituents carrying an integer charge.[12]

According to the procedure described above, σ_A constants of charged atoms and σ_G constants of charged groups, reflecting their ability to exert an inductive influence, were obtained from the basis series (Table 5).

On the basis of σ_A and σ_G values, we calculated theoretical inductive constants of charged substituents on the Taft σ^* scale (Table 4). Along with the experimental values (taken from Ref. 5 and reduced to the σ^* scale) they form a perfect linear correlation [Eqn (8)] that almost coincides with similar dependences obtained for organic (including aromatic) and organoelement substituents (Eqns (3), (6) and (7):[12]

$$\sigma^{*}_{\mathrm{theor.}} = (0.081 \pm 0.093) + (0.999 \pm 0.092)\sigma^{*}_{\mathrm{exp.}}$$
$$N = 29, r = 0.9862, S_0 = 0.310 \qquad (8)$$

Appreciable deviations of some substituents from the correlation in Eqn (8) are associated, in our opinion, with large errors in the experimental σ^* constants rather than with shortcoming of the proposed approach. This is illustrated, in particular, by the example of phosphonium substituents (Nos, 409–411 in Table 4), which are structurally similar but have considerably and randomly different $\sigma^{*}{}_{\mathrm{exp}}$ values. Thus, we may state that the model under discussion, as a whole, allows a highly accurate evaluation of the inductive effect of any organic and organoelement substituents carrying both partial and integer charges, which demonstrates its validity and wide versatility.

Since charged substituents practically complete the substituents so for known in quantitative organic chemistry and considered by us, in conclusion we give a general correlation covering all the organic, organoelement, and charged substituents:[5,12]

$$\sigma^{*}_{\mathrm{theor.}} = (0.031 \pm 0.012) + (0.993 \pm 0.006)\sigma^{*}_{\mathrm{exp.}}$$
$$N = 426, r = 0.9910, S_0 = 0.190 \qquad (9)$$

Table 6. Atomic σ_A constants, Pauling's electronegativities χ_p and 'inductive' electronegativities χ_i

Atom	σ_A	χ_p	χ_i
—F	5.88 ± 0.29	3.98	3.93
—Cl	7.62 ± 0.64	3.16	3.09
—Br	8.91 ± 0.73	2.96	2.97
—I	9.71 ± 1.24	2.66	2.80
—O—	3.25 ± 0.06	3.44	3.05
—S—	5.03 ± 0.12	2.58	2.69
—N<	1.78 ± 0.16	3.04	2.56
>C<	0.00	2.55	2.10
>C=	0.70 ± 0.14	2.75	2.25
—C≡	2.90 ± 0.58	3.29	3.13
—Se—	4.68 ± 0.98	2.55	2.54
—H	0.00	2.20	2.10
—P<	1.23 ± 0.32	2.19	2.23
—Sn<	−1.23 ± 0.50	1.96	2.02
>As—	2.38 ± 0.08	2.18	2.31
>Ge<	−0.52 ± 0.40	2.02	2.05
>B—	−0.09	2.04	2.08
—Ga<	−4.62 ± 0.30	1.81	1.75
—Hg—	−2.00 ± 0.12	2.00	1.98
—Mg—	−14.3 ± 0.04	1.31	1.29
>Si<	−0.40 ± 0.26	1.90	2.06

CRITICAL ANALYSIS OF THE MODEL AND ITS PHYSICAL MEANING

Clearly, the proposed approach to the description of inductive substituent effects in terms of Eqn (2) is in essence purely formal. At the same time, it is likely that the inverse square dependence of σ^* constants on the distance to the reactive center confirms, on the whole, the electrostatic nature of the inductive effect, reflecting the occurrence of Coulomb interactions. In this case good agreement between the theoretical and experimental inductive constants, manifesting itself in perfect correlations of the type in Eqns (3) and (6)–(9), suggests that σ_{A} constants do reflect the inductive ability of various elements, depending on their chemical nature and valence state. This, in turn, poses the question of the factors responsible for such an ability or, in other words, the physical meaning of the elementary constants σ_{A}.

To reveal the major factors that determine the nature of the σ_{A} constants, we studied the quantitative dependences of these constants on various physical and geometric parameters that are most frequently used in analyzing and rationalizing inductive interactions by means of multifactor regression analysis to obtain a number of relationships of much interest.[4] The physical parameters involved in the resulting correlations are listed in Table 6.

For example, for a large set of elements there exists a perfect correlation between σ_{A} constants, differences in electronegativity between a given element and carbon (reactive center) and squared covalent radii of elements in the corresponding valence states (all the atoms from Table 6 are included):[4]

$$\sigma_{\mathrm{A}} = (0.033 \pm 0.230) + (7.840 \pm 0.352)(\Delta_\chi + 0.45)R^2_{\mathrm{cov.}}$$
$$N = 21, r = 0.9813, S_0 = 1.013 \qquad (10)$$

where R_{cov} is the covalent radius of the corresponding atom, Δ_χ is the difference in electronegativity between this atom and carbon on the Pauling scale and 0.45 is a constant correction, depending on the electronegativity scale chosen.

The meaning of the above correction is that the 'inductive' electronegativity of a saturated carbon does not agree exactly with the Pauling scale (for which $\chi = 2.55$). If a corrected value, $\chi = 2.1$, is ascribed to carbon, then no corrections are needed, Eqn (10) being transformed into the following simple equation which describes well both the magnitude and sign of the inductive constants:

$$\sigma_{\mathrm{A}} = 7.84\Delta_\chi R^2_{\mathrm{cov.}} \qquad (11)$$

It should be noted that recalculation of the electronegativities from Eqn (11) (these are denoted χ_{I}: inductive electronegativity), which are also presented in Table 6, gives values that almost coincide with the Pauling scale (except the above-mentioned point for carbon).

From Eqns, (10) and (11) it follows that the σ_{A} constant, i.e. the inductive ability of an atom, depends not only on its electronegativity, which is undoubtedly the driving force of the electron density displacement, but is also directly proportional to the surface area of its valence shell ($R_{\mathrm{cov.}}{}^2$), i.e. to its ability to delocalize the charge being induced. Thus, the magnitude of the inductive effect of one or another element (substituent) is determined both by the 'potential difference' (Δ_χ) between this element and the reactive center and by its 'capacitance' ($R_{\mathrm{cov.}}{}^2$).

Here it is noteworthy that Eqns (10) and (11) derived here are virtually coincident with the already known[7,9,13] relationships of type (12) (see below) between the electronegativity and atomic size, which form the basis of the so-called 'geometric' electronegativity systems (e.g. the Allred–Rohow scale[9,13]), described in the common case by the following equation:

$$\chi = aZR^{-c} + b$$

Comparison of the relationships obtained shows unambiguously that the σ_{A} constants that we obtained may have the meaning of the effective charge Z of a nucleus.

Clearly, superposition of Eqns (11) and (2) gives the following final expression for the Taft inductive constant:

$$\sigma^* = 7.84 \sum_i \frac{\Delta_{\chi_i} R_i^2}{r^2} \qquad (12)$$

where $\Delta_{\chi_{\mathrm{i}}}$ is the difference in electronegativity between the ith atom of the substituent and the reactive center, R_{i} is the covalent radius of the atom and r_{i} is the distance between the atom and the reactive center.

It is noteworthy that the value of the constant term in the correlation Eqns (10–12) is nearly zero, which agrees well with mathematical expectation, since the existence of any noticeable inductive effect at $\Delta_\chi = 0$ would contradict the physical meaning of the relationship that we derived.

Equation (12) has a number of interesting consequences. First, it is clear that any substituent can be either a donor or an acceptor, depending on the nature of the reactive center, i.e. on the sign of Δ_χ. Second, the inductive effect of alkyl groups is zero only when $\Delta_\chi = 0$, i.e. when a saturated carbon atom is the reactive center (true enough, the sense is assumed by the present model).

Table 7. Theoretical $\sigma_{\mathrm{theor.}}{}^*$ and experimental $\sigma_{\mathrm{exp.}}{}^*$ values of the inductive constants of alkylcarbonylmethyl- and *trans*-carbalkoxypropenyl substituents

Substituent	Conformation	$\sigma_{\mathrm{theor.}}{}^*$	$\sigma_{\mathrm{exp.}}{}^*$
	cis	1.41	
—CH_2COR	*trans*	0.69	0.69
	cis	0.65	
—$CH{=}CHCH_2COOR$	*trans*	0.58	0.69

In the general case, a zero inductive effect of alkyls cannot be conceived in terms of our approach, especially when a heteroatom is the reactive center. With the electronegativities of carbon and hydrogen taken to be equal, Δ_χ for an alkyl substituent at any particular reactive center will always be constant and thus can be factored outside the summation sign:

$$\sigma^*_{\text{Alk.}} = \text{constant} \times \sum_i \frac{R_i^2}{r_i^2}$$

Hence the only variable in the case of alkyl substituents is the parameter $_{\mathrm{i}}(R_i^2/r_i^2)$, which describes, as was shown earlier in terms of the frontier steric effect model,[1–3] the steric shielding of the reactive center by a substituent, being in essence a measure of its steric effect. Hence it follows that there exists a genetic linear relationship (at least in terms of the proposed approach) between the inductive and steric effects of alkyls, which by no means does not confirm the ‘incorrectness’ of inductive constants of alkyls and the presence of a ‘residual steric contribution’ in these constants, as has been commonly considered.[14–17] True, for a number of reaction series, especially organic, the inductive effect of alkyls is actually nearly zero, the value of Δ_χ being insignificant.

Moreover, the inductive effect of one or another substituent is directly and essentially related to its conformation in terms of the model discussed here. In particular, the parameter r_{i}, which reflects the distance from the reactive center to each of the atoms constituting a substituent, is a conformationally sensitive parameter in Eqn (2). This confirms the proposed model, since the inductive effect depends on the conformation.[9,18]

It should be noted that comparison of the equations obtained results in a number of very interesting relationships which are beyond the scope of this paper and deserve separate, more detailed consideration. Here, it may be safely suggested that σ_{A} constants have a well defined physical meaning, which, in turn, sheds additional light on the nature of the inductive effect itself. On the other hand, the fact that the nature of Eqns (10)–(12) (which could hardly be postulated *a priori*) is fairly complex presumably accounts to a large extent for the above-mentioned numerous unsuccessful attempts to relate the inductive effect directly to electronegativity, dipole moment and other parameters of this kind.

CONCLUSION

A new model of the inductive effect has been proposed that employs the most fundamental, atomic level of additivity and allows the correct quantitative calculation of inductive constants for any substituent (organic, aromatic, organoelement and charged), using a simple and readily available system of mathematics and starting merely from its chemical structure and conformation. The elementary σ_{A} constants are determined, characterizing the inherent inductive ability of atoms, depending on their chemical nature and valence state. It is shown that these constants have a well defined physical meaning, which to a large extent elucidates the nature of inductive interactions.

REFERENCES

1. V. I. Galkin, R. D. Sayakhov and R. A. Cherkasov. *Usp. Khim.* **60,** 1617–1641 (1991).
2. V. I. Galkin and R. A. Cherkasov. *Org. Reacty. (Tartu)* **18,** 111–132 (1981).
3. V. I. Galkin, R. D. Sayakhov and R. A. Cherkasov. *Metalloorg. Khim.* **5,** 986–993 (1990).
4. V. I. Galkin, A. R. Cherkasov, R. D. Sayakhov and R. A. Cherkasov. *Russ. J. Gen. Chem.* **65** (Part II), 404–413 (1995).
5. A. R. Cherkasov, V. I. Galkin R. D. Sayakhov and R. A. Cherkasov. *Phosphorus Sulfur Silicon Relat. Elem.* **111,** 141 (1996).
6. L. Hansch and R. W. Taft. *Chem. Rev.* **91,** 165 (1991).
7. A. N. Vereshchagin. *Inductive Effect. Substituent Constants for Correlation Analysis.* Naukas, Moscow (1988) (in Russian).
8. L. V. Vilkov, V. S. Mastryukov and N. I. Sadova. *Determination of Geometric Structure of Free Molecules* Khimiya, Leningrad (1970) (in Russian).
9. A. N. Vereshchagin. *Inductive Effect* Nauka, Moscow (1987) (in Russian).
10. V. I. Galkin, A. R. Cherkasov, R. D. Sayakhov and R. A. Cherkasov. *Russ. J. Gen. Chem.* **65** (Part II), 414–418 (1995).
11. V. I. Galkin, A. R. Cherkasov, R. D. Sayakhov and R. A. Cherkasov. *Russ. Journal Gen. Chem.* **65** (Part II), 419–421 (1995).
12. V. I. Galkin, A. R. Cherkasov, R. D. Sayakhov and R. A. Cherkasov. *Russ. J. Gen. Chem.* **65** (Part II), 422–424 (1995).
13. J. E. Huheey. *Inorganic Chemistry. Principles of Structure and Reactivity,* 3rd edn. Harper and Row, New York (1983).
14. J. A. MacPhee and J. E. Dubois. *Tetrahedron Lett.,* 2471–2474 (1975).
15. M. Charton. *J. Org. Chem.* **44,** 903–906 (1979).
16. M. Charton. *J. Am. Chem. Soc.* **99,** 5687–5688 (1977).
17. D. F. de Tar. *J. Org. Chem.* **45,** 5166–5174 (1980).
18. A. N. Vereshchagin. *Structure and Reactivity of Organic Compounds* Nauka, Moscow (1978) (in Russian).