Determination of Constants of Anionic Substituents based on Nitrile Infrared Frequencies and Intensities

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A new approach, based on dual-parameter correlation equations, for the determination of σ^+ and other substituent constants is described; it consists of the simultaneous use of data for a given substituent, obtained from at least two different series. Constants of 14 negatively charged substituents have been calculated on the basis of Yukawa–Tsuno-type correlations of nitrile i.r. frequencies and intensities, measured in polar aprotic solvents. The reliability of the constants of anionic substituents, thus obtained, is exemplified in series of carbonyl frequencies of ketones and esters.

Correlations of frequencies (ν_{CN}) and integrated intensities (A_{CN}) of the nitrile stretching bands of substituted benzonitriles have been studied repeatedly.[1] These spectroscopic features have been recommended and/or used for the determination of various substituent constants (see *e.g.* refs. 2 and 3 and references therein).

Determination of σ^+ constants of anionic substituents by the standard chemical method [4] is obviously impossible. It has been recently reported that even reliable σ° values of charged (both anionic and cationic) substituents cannot be determined by this method.[5] This result has been considered to indicate that charged substituents do not obey Hammett-type relationships.[5] One should point out, however, that the reactivity of ionic species is extremely sensitive to ionic aggregation,[6] and the latter is a complex function of the solvent, concentration, counterion, *etc.*[6] On the other hand, carbonyl, nitrile, and other i.r. frequencies of ionic species are fairly independent of the solvent and/or counterion.[7] We believe, therefore, that an i.r. spectroscopic approach to the determination of constants of charged substituents could be a reasonable alternative.

The aim of this paper is to describe the determination of σ^+,σ°, and $\Delta\sigma_R{}^+$ constants of a series of anionic substituents on the basis of correlations of nitrile i.r. frequencies and intensities of substituted benzonitriles in polar aprotic solvents.

Results and Discussion

The ν_{CN} and A_{CN} values for 60 substituted (45 neutral) benzonitriles are listed in Table 1 and the results of the statistical treatment of the data for the neutral compounds, according to the equations of Brown and Okamoto,[4] Yukawa and Tsuno,[8] and Taft [9,10] [equations (1)—(3), respectively] are given in Table 2.

$$Y = \rho\sigma^+ + b \qquad (1)$$

$$Y = \rho(\sigma^\circ + r'\Delta\sigma_R{}^+) + b \qquad (2)$$

$$Y = \rho_I\sigma_I + \rho_R\sigma_R{}^+ + b \qquad (3)$$

A comparison of the resulting correlation factors (Table 2) with those already known [3,11] and the results of the statistical treatment of the literature data for CCl_4 and other solvents [12] indicates that the use of dimethyl sulphoxide (DMSO) and hexamethylphosphoramide (HMPA) instead of the usual spectroscopic solvents does not change significantly the relative accuracy of the studied correlations. This fact is essential because benzonitriles with anionic substituents can be easily generated in polar aprotic solvents only.

In order to evaluate σ^+ constants of the studied charged substituents by the usual method, one should substitute any of the ν_{CN} or $A^{\frac{1}{2}}{}_{CN}$ values of a given anion in the corresponding correlation equation from Table 2 and solve it with respect to σ^+; the errors of these σ^+ values can be estimated by simultaneously taking into account the errors in the slopes and intercepts, and the experimental errors. This method gave, for example, for the substituent 4-O$^-$ from the four experimental results and correlation equations 3, 4, 7, and 8 (Table 2) the values -5.5 ± 0.4, -4.9 ± 0.3, -3.4 ± 0.2, and -3.7 ± 0.2. Having in mind the value of -2.3 reported previously,[13] one can see that there is no consistency within the values obtained from different definition series. We should note, however, that a strong sensitivity with respect to the definition series is characteristic of all σ-constants, for all the substituents (both neutral and charged); the differences between their values, given by different definition series for the same substituent, are considerably larger than the estimated errors (*cf.* refs. 5, 13, and 14, and the above example).

One can deduce, therefore, that the origin of these variances is not the experimental errors or the low accuracy of the corresponding correlations, but they are rather results of the different contributions of induction and resonance to the total substituent effects in the different series. This statement is important because it suggests that a direct determination of σ-constants in any series different from the standard one (of the corresponding type of constants) is not justified. The use of mean values is not justified either, as it has been shown [14] that the different-series σ-constants show no tendency to converge to the standard values of σ, σ^+, or σ^-.

We tend to believe that a rational approach to the problem is to account for the different ratios of constituents of the total substituent effects by use of dual-, or, occasionally multi-parameter relationships, and to express *e.g.* σ^+ as $\sigma^+ = \sigma^\circ + \Delta\sigma_R{}^+$ (Yukawa and Tsuno) or $\sigma_p{}^+ = \sigma_I + \sigma_R{}^+$ (Taft). The former expression has the advantage of providing both $\sigma_{para}{}^+$ and $\sigma_{meta}{}^+$; in addition to this we should mention that a recent analysis [15] has indicated that the Yukawa–Tsuno equation is physically better justified (for the case of benzene derivatives) than that of Taft.

To obtain reliable substituent constants, we decided to use all the data available for ν_{CN} and $A^{\frac{1}{2}}{}_{CN}$ simultaneously, to construct systems of four (Yukawa–Tsuno) or eight (Taft) equations with two unknowns, and to solve them by the least-squares method. The σ° and $\Delta\sigma_R{}^+$ values are given in Table 3; σ_I and $\sigma_R{}^+$ thus obtained seem to be less reliable (*cf.* the following examples). To estimate the error intervals of each constant, we used the values of s_ρ, s_b for the corresponding dual-parameter correlations, and the experimental errors. We obtained, for example, for the 4-O$^-$ substituent: σ° -2.55 to -2.93, $\Delta\sigma_R{}^+$ -1.16 to -1.83, σ_I -0.33 to -1.38, and $\sigma_R{}^+$ -2.53 to -3.45.

Table 1. Frequencies (cm^{-1}) and integrated intensities ($l\ mol^{-1}\ cm^{-2}$) of the nitrile stretching bands of substituted benzonitriles in hexamethylphosphoramide (HMPA) and dimethyl sulphoxide (DMSO)

		ν_{CN}		A_{CN}	
No.	Substituents	HMPA	DMSO	HMPA	DMSO
A Benzonitriles with neutral substituents					
1	H	2 226.7	2 227.4	3 510	4 720
2	3-Methyl	2 227.3	2 227.3	3 820	4 670
3	4-Methyl	2 226.4	2 226.6	5 190	6 090
4	3,5-Dimethyl	2 229.5 [a]	2 230.0 [a]	3 790	5 060
5	4-Isopropyl	2 224.9	2 226.0	1 960 [a]	5 810
6	3-Phenyl	2 228.3	2 228.6	4 030	4 120
7	4-Phenyl	2 225.2	2 226.8	5 740	5 930
8	3-Trifluoromethyl	2 233.8	2 234.7	2 500	2 800
9	4-Trifluoromethyl	2 231.6	2 232.9	1 760	2 510
10	4-Ethoxycarbonylmethyl	2 227.0	2 229.0	5 000	6 580
11	3-Cyano	2 234.3	2 235.0	2 220 [b]	3 170 [b]
12	4-Cyano	2 230.0	2 231.4	1 870 [b]	2 850 [b]
13	3,5-Dicyano	2 242.7	2 244.2	1 220 [b]	1 600 [b]
14	4-Formyl	2 228.7	2 230.6	2 720	3 360
15	3-Acetyl	2 230.2	2 231.3	3 100	3 320
16	4-Acetyl	2 229.1	2 230.3	2 810	2 980
17	4-Benzoyl	2 229.0	2 230.8	2 430	2 170
18	3-Carboxy	2 231.0	2 233.1	2 650	3 190
19	4-Carboxy	2 229.5	2 230.5	3 690	3 650
20	3-Ethoxycarbonyl	2 231.6	2 232.5	2 670	2 980
21	4-Ethoxycarbonyl	2 229.4	2 230.5	2 970	3 150
22	3-Fluoro	2 232.6	2 233.1	2 920	3 020
23	4-Fluoro	2 229.5	2 230.3	3 840	4 480
24	3-Chloro	2 231.3	2 231.8	2 880	3 580
25	4-Chloro	2 229.2	2 230.1	3 830	4 710
26	3-Bromo	2 230.7	2 231.7	2 790	3 830
27	4-Bromo	2 228.5	2 229.5	4 100	4 960
28	3-Aza	2 231.3	2 232.2	2 560	3 250
29	4-Aza	2 235.2	2 236.8	1 040	1 340
30	3-Amino	2 223.2	2 224.4	4 940	5 720
31	4-Amino	2 205.7 [a]	2 207.4 [a]	17 000	17 200
32	3-Dimethylamino	2 224.3	7 224.9	5 500	6 640
33	4-Dimethylamino	2 212.1	2 211.4	18 300	20 000
34	3-Acetylamino	2 227.3	2 230.3	3 230	3 930
35	4-Acetylamino	2 221.3	2 222.5	8 780	9 200
36	4-Benzoylamino	2 221.2	2 222.2	6 450	8 520
37	3-Nitro	2 235.1	2 235.6	1 960	2 770
38	4-Nitro	2 232.1	2 233.3	1 130	1 720
39	3,5-Dinitro	2 241.8	2 243.1	967	1 380
40	3-Hydroxy	2 226.3	2 229.0	4 600	5 030
41	4-Hydroxy	2 220.1	2 221.2	10 300	12 100
42	3-Methoxy	2 228.6	2 228.5	3 550	4 400
43	4-Methoxy	2 223.0	2 223.2	8 170	9 080
44	3,5-Dimethoxy	2 228.1	2 228.7	3 470	4 060
45	4-Methylsulphonyl	2 231.0	2 233.0	2 490	2 550
B Benzonitriles with anionic substituents					
46	3-CO_2^-	2 224.7	2 226.9	4 040	4 610
47	3-$NCHC^-$	2 217.6	2 219.0	7 200	9 250
48	3-CH_3CON^-	2 218.5	2 220.2	5 480	7 520
49	3-O^-	2 213.4	2 214.8	7 930	7 980
50	4-CO_2^-	2 222.9	2 224.5	5 960	7 030
51	4-$CH_2CO_2^-$	2 222.9	2 224.0	6 200	8 860
52	4-O_2NHC^-	2 205.6	2 211.2	24 200	24 000
53	4-$NCHC^-$	2 179.4	2 180.5	35 200	39 600
54	4-EtO_2CHC^-	2 181.1	2 183.8	51 100	58 000
55	4-$(O_2CHC)^{2-}$	2 157	2 161.8		97 000
56	4-H_2C^-	2 137			
57	4-CH_3CON^-	2 200.6	2 203.5	31 200	31 000
58	4-$C_6H_5CON^-$	2 200.8	2 204.1	31 700	29 000
59	4-NH^-	2 166	2 170.5		72 000
60	4-O^-	2 186.9	2 188.2	39 400	45 000

[a] Excluded from the statistical treatment. [b] Calculated for one nitrile group.

Table 2. Correlations of ν_{CN} and $A^{\frac{1}{2}}_{CN}$ of benzonitriles with neutral substituents with substituent constants, according to the equations of Brown and Okamoto, Yukawa and Tsuno, and Taft [equatons (1)—(3)]

No.	Y	Solvent	Series	Slope		s_p	b	s_b	$\pm r$	S.d.	n
I According to Brown and Okamoto											
1	ν_{CN}	HMPA	*m*	12.14		0.53	2 226.8	0.3	0.9843	0.9	21
2	ν_{CN}	DMSO	*m*	12.64		0.58	2 227.7	0.3	0.9803	1.0	21
3	ν_{CN}	HMPA	*p*	7.32		0.40	2 226.8	0.3	0.9581	1.5	23
4	ν_{CN}	DMSO	*p*	8.00		0.39	2 227.8	0.2	0.9672	1.4	23
5	$A^{\frac{1}{2}}_{CN}$	HMPA	*m*	−24.55		0.95	62.2	0.5	0.9624	2.8	21
6	$A^{\frac{1}{2}}_{CN}$	DMSO	*m*	−25.05		0.96	68.3	0.5	0.9587	3.0	22
7	$A^{\frac{1}{2}}_{CN}$	HMPA	*p*	−38.81		0.75	68.4	0.5	0.9775	6.0	23
8	$A^{\frac{1}{2}}_{CN}$	DMSO	*p*	−38.05		0.69	72.1	0.5	0.9816	5.2	24
II According to Yukawa and Tsuno											
				r'	ρ						
9	ν_{CN}	HMPA	*m* and *p*	0.729	10.23	0.44	2 226.7	0.2	0.9424	1.9	39
10	ν_{CN}	DMSO	*m* and *p*	0.737	10.75	0.42	2 227.7	0.2	0.9549	1.7	39
11	$A^{\frac{1}{2}}_{CN}$	HMPA	*m* and *p*	1.856	−25.25	0.37	62.4	0.3	0.9833	4.2	40
12	$A^{\frac{1}{2}}_{CN}$	DMSO	*m* and *p*	1.760	−25.22	0.35	67.7	0.3	0.9878	3.4	41
III According to Taft											
				ρ_I	ρ_R						
13	ν_{CN}	HMPA	*m*	11.60	2.75	0.51	2 227.4	0.3	0.9847	0.9	20
14	ν_{CN}	DMSO	*m*	12.10	2.67	0.51	2 228.1	0.3	0.9864	0.8	20
15	ν_{CN}	HMPA	*p*	7.60	7.08	0.46	2 226.6	0.3	0.9591	1.4	19
16	ν_{CN}	DMSO	*p*	8.46	7.60	0.46	2 227.6	0.3	0.9569	1.4	19
17	$A^{\frac{1}{2}}_{CN}$	HMPA	*m*	−21.77	−6.93	0.72	60.4	0.4	0.9773	2.3	21
18	$A^{\frac{1}{2}}_{CN}$	DMSO	*m*	−21.05	−7.75	0.68	65.6	0.7	0.9781	2.3	21
19	$A^{\frac{1}{2}}_{CN}$	HMPA	*p*	−33.59	−38.66	0.69	66.0	0.6	0.9796	5.8	19
20	$A^{\frac{1}{2}}_{CN}$	DMSO	*p*	−27.95	−39.41	0.49	68.5	0.5	0.9887	4.2	20

s_p, Standard deviation of the slope; s_b, standard deviation of the intercept; r, correlation coefficient; s.d., standard deviation; n, number of the data points; m, *meta*-series; p, *para*-series.

Table 3. Constants of anionic substituents, derived from the Yukawa–Tsuno equation, by simultaneous least-squares treatment

Substituents	σ°	$[\Delta\sigma_R^+]$	σ^+	Limits
$3\text{-}CO_2^-$	−0.19	0.09	−0.10	−0.03 −0.15
3-NCHC$^-$	−0.81	−0.11	−0.92	−0.80 −0.99
$3\text{-}CH_3CON^-$	−0.93	0.18	−0.75	−0.64 −0.84
3-O$^-$	−1.38	0.23	−1.15	−1.03 −1.30
$4\text{-}CO_2^-$	−0.16	−0.25	−0.41	−0.32 −0.71
$4\text{-}CH_2CO_2^-$	−0.15	−0.38	−0.53	−0.45 −0.58
$4\text{-}O_2NHC^-$	−0.50	−1.69	−2.19	−2.02 −2.35
4-NCHC$^-$	−4.16	−0.50	−4.67	−4.38 −5.07
$4\text{-}EtO_2CHC^-$	−2.86	−2.13	−5.00	−4.49 −5.24
$4\text{-}(O_2CHC)^{2-}$	−3.85	−3.32	−7.17	−6.76 −7.79
$4\text{-}CH_3CON^-$	−0.96	−1.92	−2.90	−2.68 −3.23
$4\text{-}C_6H_5CON^-$	−0.87	−1.91	−2.77	−2.58 −2.88
4-HN$^-$	−3.98	−2.25	−6.23	−5.77 −6.89
4-O$^-$	−2.67	−1.59	−4.27	−3.99 −4.53
$4\text{-}H_2C^-$			−11.2 (ref. 3)	

The values of σ^+ given in Table 3 are sums of the corresponding σ° and $\Delta\sigma_R^+$ values, but their error intervals cannot be calculated by simple summation. The analysis of the errors of σ^+, given in some detail in the Experimental section, demonstrates that the variations in these values tend to compensate each other. So, the errors of σ^+ values are smaller than the sums of the errors of their components. Let us consider again the case of the 4-O$^-$ substituent: σ^+ −3.2 to −5.9 from single-parameter correlations, σ^+ −2.9 to −4.8 from Taft-type correlations, taking into account the sum of errors, σ^+ −3.7 to −4.8 from Yukawa–Tsuno-type correlations, taking into account the sum of errors, and σ^+ −4.0 to −4.5 from Yukawa–Tsuno-type correlations, taking into account the error analysis.

We thus consider that the dual- (and, possibly, multi-) parameter approach to the determination of substituent constant is more promising than the usual single-parameter one.

Conclusions.—The method suggested in this paper yielded 14 sets of σ°, $\Delta\sigma_R^+$, and σ^+ constants for anionic substituents. They are fairly self-consistent: the correlation coefficients of both ν_{CN} and $A^{\frac{1}{2}}_{CN}$ are $r > 0.99$ for both the single-parameter (σ^+) and Yukawa–Tsuno-type correlations for the whole series of benzonitriles with both neutral and anionic substituents.

We hope the present set of substituent constants will prove suitable for correlations of other properties of molecules with charged substituents. The application of these constants to carbonyl frequencies and intensities is now being studied in our laboratory. Also, by increasing the number of the definition series and applying the same approach, one could increase the statistical reliability of the constants for anionic substituents.

Experimental

Commercially non-available nitriles were prepared and purified according to the literature. The anions were prepared by metallation of the corresponding conjugate acids with dry sodium methoxide. This reagent proved ineffective for the anions 55, 56, and 59 (Table 1). The first two were obtained by metallation with dimsyl sodium (in DMSO) and naphthalene disodium (in HMPA); anion (59) was prepared in the latter manner only. The i.r. spectra were recorded on UR-20 and (independently) on IR-75 Carl Zeiss spectrophotometers in CaF_2 cells of 0.06—0.24 mm path length. The integrated intensities were calculated by direct integration. The reproducibility was ± 0.3 cm^{-1} for ν_{CN} and *ca.* 5% for A_{CN}.

Calculations.—The solution of the least-square problem involving four or eight equations with two unknowns (4.2 or 8.2 systems) was done by symmetrization of the matrix **B** in $\mathbf{B}\,.\,\mathbf{x} = \mathbf{a}$, where **B** is the matrix of regression coefficients taken from Yukawa–Tsuno- or Taft-type equations, **x** is the column vector of unknowns, and **a** is the column vector of the differences $\nu - b_\nu$ and $A^{\frac{1}{2}} - b^{\frac{1}{2}}_A$ for the given substituent, by multiplication by $\mathbf{B}^*$ (**B** transposed) $\mathbf{B}^*\,.\,\mathbf{B}\,.\,\mathbf{x} = \mathbf{B}^*\,.\,\mathbf{a}$ the system arising, of two equations with two unknowns, was solved to obtain the required pair of substituent constants σ° and $\Delta\sigma_R^+$, or σ_I and σ_R^+.

The analysis of the errors of these constants (for 4.2 systems) arising from experimental errors, s_ρ and s_b, reveals that σ° becomes larger when $\Delta\sigma_K^+$ decreases, *i.e.* these errors compensate for each other in the value of σ^+. The largest (algebraic) values of σ^+ were found for overestimated frequencies (by both experimental errors and s_b), underestimated intensities, and overestimated (absolute values of) slopes of the dual-parameter correlations. They are given as upper threshold values of σ^+ constants in Table 3. The smallest values of σ^+ were produced by underestimated frequencies and slopes, and overestimated intensities. The set of these values constitutes the lower threshold of σ^+ constants in Table 3. The largest values of σ° were found for underestimated frequencies, overestimated intensities, and nominal slopes of the starting regressions. This case gives simultaneously the smallest values of $\Delta\sigma_R^+$. The smallest values of σ° appear for underestimated experimental data for both ν_{CN} and $A^{\frac{1}{2}}_{CN}$, and nominal slopes. This case demonstrates again the tendency for compensation of the variations of σ° and $\Delta\sigma_R^+$.

Checking the Reliability.—We had the opportunity to check the reliability of the constants of some substituents from Table 3 on the basis of ν_{CO}–σ^+ correlations for compounds RC_6H_4COX [X = CH_3O, C_2H_5O, CH_3, and $R'C_6H_4$, equations (4)—(7); solvent DMSO] and ν_{CO} data (the same solvent) for some anions with the same general formula we recently obtained.[16]

$$\text{methyl benzoates } \nu_{CO} = 10.27\,\sigma^+ + 1\,720.1 \qquad r\ 0.987,\ \text{s.d. } 1.1,\ n\ 17 \tag{4}$$

$$\text{ethyl benzoates } \nu_{CO} = 10.51\,\sigma^+ + 1\,714.1 \qquad r\ 0.992,\ \text{s.d. } 0.9,\ n\ 17 \tag{5}$$

$$\text{acetophenones } \nu_{CO} = 13.49\,\sigma^+ + 1\,681.8 \qquad r\ 0.990,\ \text{s.d. } 1.2,\ n\ 23 \tag{6}$$

$$\text{benzophenones } \nu_{CO} = 9.64\,\sigma^+ + 1\,657.7 \qquad r\ 0.980,\ \text{s.d. } 1.9,\ n\ 44 \tag{7}$$

For example, we found the following results for the cases of 3-O^- and 4-O^-(substituent, equation, calculated ν_{CO}, experimental ν_{CO}): 3-O^-, 4, 1 708.8, 1 705.9; 4-O^-, 4, 1 676.2, 1 679.1; 3-O^-, 5, 1 702.0, 1 703.1; 4-O^-, 5, 1 669.2, 1 673.7; 3-O^-, 6, 1 666.3, 1 666.8; 4-O^-, 6, 1 624.2, 1 630.0; 3-O^-, 7, 1 646.6, 1 644.5; 4-O^-, 7, 1 616.5; 1 611.8. So, the deviations for the 3-O^- case are maximum 2.4 cm^{-1}, mean 0.7 cm^{-1}; for the 4-O^- case are maximum 5.8 cm^{-1}, mean 2.1 cm^{-1}. Compared to the whole intervals of variations of ν_{CO} in these carbonyl series (compounds with both neutral and anionic substituents), *viz.* methyl and ethyl benzoates, 65 cm^{-1}; acetophenones, 75 cm^{-1}; benzophenones, 110 cm^{-1}, the above deviations seem to be quite acceptable. For comparison, if the value for σ^+ 4-O^- of -2.3, taken from ref. 13, is substituted into equations (4)—(7), the deviations will be maximum 23.7 cm^{-1}, mean 19.5 cm^{-1}.

Acknowledgements

We thank Dr. I. Pojarlieff, Institute of Organic Chemistry, Bulgarian Academy of Sciences, for a critical reading of the manuscript and some valuable suggestions. Thanks are due also to Dr. V. Dimitrov, same Institute, for some useful advice.

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Received 25th *March* 1982; *Paper* 2/520