

SUBSTITUENT EFFECTS IN INFRARED SPECTROSCOPY. III.*
 FREQUENCIES AND INTENSITIES OF THE C≡N BAND
 IN *meta*- AND *para*- SUBSTITUTED BENZONITRILES

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Frequencies and intensities of the C≡N stretching vibration of seventy-one *meta*- and *para*-substituted benzonitriles and of eighteen polyderivatives have been measured in chloroform solution. The frequencies of *para*-derivatives containing acceptor substituents depend upon electronic substituent effects as expressed by the Hammett constants σ_p ($\rho = 7.6 \text{ cm}^{-1}$); with donor substituents the mesomeric effect comes into play and can be approximately represented by the σ_p^+ constants. All *meta*-derivatives show higher frequencies than expected from their electronic substituent effects as expressed by the σ_m ; this effect is independent of the nature of substituent, its mass or the symmetry of the molecule (*meta*-effect). The intensities of *meta*- as well as of *para*-derivatives depend only upon electronic, particularly mesomeric effects, and can be correlated by σ^+ constants.

In this series of papers we examine the effects of substituents upon infrared frequencies and intensities on a broader and more systematically chosen experimental basis than hitherto, and we attempt to resolve these effects into individual components^{1,2}. *Meta*- and *para*-benzene derivatives have been often used as model compounds to which the Hammett equation (1) and also equation (2) derived by us³ can be applied. The latter is valid for substituents without an alpha free-electron pair and relates their effects to the *meta*- and *para*-positions.

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

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

In previous communications we investigated the pattern of carboxylic O—H stretching frequencies in substituted benzoic acids¹ and characteristic frequencies (ν_s , ν_{as} , γ , δ) of the NO₂ group in substituted nitrobenzenes². While the former is controlled only by electronic effects of substituents, both equations (1) and (2) being fulfilled¹, the latter are affected, to a greater or lesser degree, by other factors².

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This paper is devoted to a study of the stretching frequency of the C≡N triple bond in substituted benzonitriles, which is both highly characteristic and little dependent on mass and combination effects, and can be easily identified and measured with a considerable accuracy. The latter advantage is partly impaired by the rather low sensitivity to substituents effects. On the other hand the advantageous position of the absorption band, placed as it is far from other bands, facilitates intensity measurement and makes substituted benzonitriles an ideal subject for study. All existing studies⁴⁻¹⁶ have a common shortcoming from the point of view indicated in our introductory paper¹, that is to say only a small number of unsystematically chosen derivatives have been investigated. Furthermore, sometimes even standard conditions have not been maintained. We feel that neither the care paid exceptionally to the choice of compounds¹⁰ can compensate for their insufficient number.

During our work it became necessary to test certain regularities using di- and tri-substituted derivatives. Hence polyderivatives 70-87 (Table I) were added to our set of *meta*- and *para*-derivatives 1-69; a more detailed investigation of poly-substitution was, however, not intended nor envisaged.

EXPERIMENTAL AND RESULTS

Materials

Substituted benzonitriles 1-89 (Table I) were purified by standard methods. In the main, compounds were prepared according to literature procedures¹⁷⁻³⁹ or by applying known methods. Many nitriles were prepared from the corresponding aldehydes *via* the oxime^{35,36}; the products were purer than those obtained from Sandmeyer reactions. The method of heating the carboxylic acid with benzenesulfonamide³¹ was also employed several times with relative success. In no case were attempts made to find optimum reaction conditions or to maximise yields. Characteristic physical constants for our samples were in general agreement with literature data; references are given in Table I only for less common compounds, in particular those not listed in Beilstein. Melting points are corrected.

S-(3-Cyanobenzyl)isothiuronium chloride (8). A solution of α -chlorotolunitrile (1.51 g, 0.01 mol) and thiourea (0.76 g, 0.01 mol) in ethanol (5 ml) was refluxed 30 min, crystals deposited upon cooling were collected, yield 1.78 g (78%), m.p. 200°C (ethanol). For C₉H₁₀ClN₃S (227.7) calculated: 15.57% Cl, 18.44% N; found: 15.45% Cl, 18.48% N. S-(4-Cyanobenzyl)isothiuronium chloride (9) was prepared by the same procedure as for the 3-isomer, yield 80%, m.p. 201°C (ethanol). For C₉H₁₀ClN₃S (227.7) calculated: 15.57% Cl, 18.44% N; found: 15.56% Cl, 18.42% N. The compound was prepared as an intermediate⁴⁶. Phenyl 3-cyanobenzoate (32). To a solution of NaOH (0.8 g) and phenol (0.94 g, 0.01 mol) in water (15 ml) 3-cyanobenzoyl chloride (1.66 g, 0.01 mol) was added, the mixture was shaken 30 min, the product collected and washed with water, yield 1.60 g (72%), m.p. 94°C (cyclohexane). For C₁₄H₉NO₂ (223.2) calculated: 75.33% C, 4.06% H, 6.27% N; found: 75.46% C, 4.26% H, 6.53% N. Phenyl 4-cyanobenzoate (33) was prepared in the same way as the 3-isomer^{47,48}, yield 77%, m.p. 87°C (cyclohexane). 3-Cyanophenyl-trimethylammonium iodide (44). A solution of 3-cyano-N,N-dimethylaniline²⁸ (0.73 g, 0.005 mol), methyl iodide (2 g) and methanol (3 drops) in benzene (1 ml) has been left two weeks at laboratory temperature protected before light and moisture. Deposited crystals were collected and washed

TABLE I
 Frequency (cm^{-1}) and Intensity ($10^3 \text{ mol}^{-1} \text{ l cm}^{-2}$) of the $\text{C}\equiv\text{N}$ Stretching Vibration of Substituted (R) Benzonitriles (in chloroform)

No	R	M.p., $^{\circ}\text{C}$	Ref.	$\nu(\text{C}\equiv\text{N})$	<i>A</i>	Constant σ (ref. ^{3,40})
1	H	1.5280 ^a	—	2 230.5 ^b	2.83 ^c	0
2	3-CH ₃	1.5254 ^a	—	2 231.5	3.85	-0.10
3	4-CH ₃	30	—	2 229.8	4.68	-0.15
4	3-CH ₂ C ₆ H ₅	1.5869 ^a	3	2 231.8	3.64	-0.08
5	4-CH ₂ C ₆ H ₅	48	17	2 230.1	5.16	-0.09
6	3-CH ₂ OC ₆ H ₅	51	18	2 233.0	2.00	0.06
7	4-CH ₂ OC ₆ H ₅	65	18	2 231.2	4.42	0.07
8	3-CH ₂ SC(NH ₂) ₂ ⁺ Cl ⁽⁻⁾	200	^d	2 232.9 ^e	—	0.13 ^f
9	4-CH ₂ SC(NH ₂) ₂ ⁺ Cl ⁽⁻⁾	201	^d	2 234.0 ^e	—	0.15 ^f
10	3-CH ₂ SO ₂ C ₆ H ₅	162	3	2 235.0	2.88	0.15
11	4-CH ₂ SO ₂ C ₆ H ₅	207	19	2 232.5 ^e	—	0.17
12	3-CH ₂ Cl	69	—	2 234.7	2.98	0.11
13	4-CH ₂ Cl	80	—	2 233.1	3.87	0.12
14	3-CH ₂ Br	94	18	2 234.2	3.04	0.12
15	4-CH ₂ Br	115	18	2 232.5	3.52	0.14
16	3-CH ₂ I	114 ^g	20	2 233.8	3.39	0.10
17	4-CH ₂ I	144	21	2 231.8	4.51	0.11
18	3-CF ₃	1.4535 ^a	22	2 237.7	1.80	0.46
19	4-CF ₃	39	22	2 235.7	1.64	0.53
20	3-C ₆ H ₅	48	—	2 232.8	3.18	0.06
21	4-C ₆ H ₅	84	—	2 229.6	5.30	0.03
22	3-CHO	78	—	2 236.8	2.26	0.36 ^g
23	4-CHO	102	—	2 234.0	^h	0.43 ^g
24	3-COCH ₃	99	—	2 235.0	2.53	0.36
25	4-COCH ₃	59	—	2 233.5	2.37	0.44
26	3-COC ₆ H ₅	90	23	2 236.0	2.60	0.34
27	4-COC ₆ H ₅	112	23	2 234.5	2.58	0.42
28	3-COOH	219	3	2 235.8	(3.80) ^h	0.35
29	4-COOH	218	3	2 235.0	1.93	0.42
30	3-COOCH ₃	61	24	2 235.5	2.53	0.36
31	4-COOCH ₃	67	25	2 232.2	(3.6) ^h	0.43
32	3-COOC ₆ H ₅	94	^d	2 236.0	2.11	0.37 ^f
33	4-COOC ₆ H ₅	87	^d	2 233.8	2.122	0.44 ^f
34	3-CONH ₂	223	26	2 236.2	^h	0.35 ^f
35	4-CONH ₂	224	25	2 234.5	^h	0.43 ^j
36	3-COCl	42	26	2 238.8	1.75	0.46 ^f
37	4-COCl	65	25	2 235.5	1.45	0.52 ^f
38	3-CN	162	—	2 239.0	(1.88) ^{h,k}	0.61
39	4-CN	223	—	2 235.3 ^e	(1.55) ^{h,k}	0.69
40	3-NH ₂	54	27	2 232.5	4.05	-0.15

TABLE I
 (Continued)

No	R	M.p., °C	Ref.	$\nu(\text{C}\equiv\text{N})$	A	Constant σ (ref. 3,40)
41	4-NH ₂	86	27	2 221.0	11.0 ^h	-0.66
42	3-N(CH ₃) ₂	26	28	2 231.0	4.05	-0.20
43	4-N(CH ₃) ₂	75	28	2 215.0 ^l	15.0 ^{h,l}	-0.82
44	3-N(CH ₃) ₃ ⁽⁺⁾ I ⁻	184	d	2 235.5 ^m	—	0.88 ⁿ
45	4-N(CH ₃) ₃ ⁽⁺⁾ I ⁻	151	d	2 230.8 ^m	—	0.82 ⁿ
46	3-NHCOCH ₃	131	28	2 233.5	3.34	0.12
47	4-NHCOCH ₃	204	28	2 228.7 ^e	—	-0.09
48	3-NO ₂	118	—	2 239.5 ^o	1.50 ^p	0.70
49	4-NO ₂	148	—	2 236.5 ^q	1.26 ^r	0.80
50	3-OH	81	—	2 234.5	^h	0.09
51	4-OH	112	—	2 226.5	9.44	-0.33
52	3-OCH ₃	23	30	2 232.7	2.56	0.12
53	4-OCH ₃	60	—	2 226.7	7.30	-0.26
54	3-OCOCH ₃	61	—	2 235.5	2.56	0.26
55	4-OCOCH ₃	58	—	2 232.0	2.14	0.16
56	3-SO ₂ CH ₃	105	31	2 238.0	(1.59)	0.64
57	4-SO ₂ CH ₃	142	31	2 236.5	(1.54)	0.73
58	3-SO ₂ NH ₂	153	32	2 237.8 ^e	—	0.53
59	4-SO ₂ NH ₂	169	32	2 236.2 ^e	—	0.60
60	3-SO ₂ Cl	51	32	2 239.5	0.85	0.87 ^f
61	4-SO ₂ Cl	110	32	2 238.6	1.08	1.00 ^f
62	3-F	1.5063 ^a	—	2 235.8	1.91	0.36
63	4-F	36	—	2 232.7	4.03	0.05
64	3-Cl	41	—	2 235.3	2.52	0.38
65	4-Cl	92	—	2 233.0 ^s	3.45 ^t	0.23
66	3-Br	39	—	2 235.0	2.14	0.39
67	4-Br	113	—	2 232.5	3.78	0.23
68	3-I	40	31	2 234.3	2.58	0.34
69	4-I	127	31	2 231.5	3.94	0.19
70	3,5-(CH ₃) ₂	44	33	2 233.2	3.89	-0.20
71	3,5-(CN) ₂	253	^u	2 248.0 ^e	—	1.22
72	3,5-(NH ₂) ₂	194	^d	2 230.5 ^e	^h	-0.30
73	3,5-(NHCOCH ₃) ₂	299	^d	(2 235.5) ^m	—	0.24
74	3,5-(NO ₂) ₂	130	34	2 245.5 ^e	—	1.40
75	3,5-Cl ₂	66	^d	2 239.6	1.91	0.76
76	3,5-Br ₂	97	^d	2 237.4	1.73	0.78
77	3,4-(CH ₃) ₂	67	—	2 230.0	5.11	-0.25
78	3,4-benzo	67	—	2 229.3	5.02	0.04 ⁿ
79	3,4-(OCH ₃) ₂	68	35	2 228.0	6.47	-0.14
80	3,4-OCH ₂ O-	93	36	2 230.5	^h	-0.16 ^o
81	3-OCH ₃ -4-OH	89	36	2 227.0	6.90	-0.21

TABLE I
 (Continued)

No	R	M.p., °C	Ref.	$\nu(\text{C}\equiv\text{N})$	A	Constant σ (ref. ^{3,40})
82	3-OCH ₃ -4-OCOCH ₃	110	36	2 233.2	3.73	0.28
83	3,4-Cl ₂	72	37	2 236.5	2.72	0.61
84	3-Br-4-OH	155	38	2 231.0 ^e	—	0.06
85	3-Br-4-OCOCH ₃	98	38	2 234.2	^h	0.55
86	3,5-Cl ₂ -4-NH ₂	120	^d	2 231.5	^h	0.10
87	3,5-Br ₂ -4-NH ₂	124	39	2 228.0	5.48	0.12
88	3-aza	50	31	2 235.5	2.12	0.62 ^v
89	4-aza	80	31	2 240.0 ^w	0.85 ^w	0.93 ^v

^a n_{D}^{20} ; ^b ref.^{5,8,10,12,13,16} give 2231, 2230, 2231 (in C₂Cl₄), 2230.6, 2234, and 2233 cm⁻¹, resp.; ^c ref.^{5,7,8,10,14,16} give 3.74, 3.5, 3.16, 2.9 (in C₂Cl₄ solution), 3.60 and 4.30 10³ mol⁻¹ l cm⁻¹; ^d see Experimental; ^e in the saturated solution; ^f estimated values; for substituents COCl and SO₂Cl the estimate is based on the relation³ to constants σ_1 in weakly protic solvent⁴²; ^g cf. ref.⁴¹; ^h strongly asymmetrical band; ^j cf. ref.⁴³; ^k corrected by the statistical factor; ^l ref.^{6,12,13} give the frequencies 2 224, 2216.1, and 2217 cm⁻¹ resp., and intensity⁶ 17.5 10³ mol⁻¹ l cm⁻²; ^m in Nujol suspension; ⁿ cf. ref.⁴⁴; ^o ref.^{5,8,10} give 2239, 2242, and 2238.5 cm⁻¹ (in C₂Cl₄) cm⁻¹; ^p Ref.^{5,8,10} give 1.75, 1.65, and 1.25 (in C₂Cl₄) 10³ mol⁻¹ l cm⁻²; ^q Ref.^{5,8,10,13} give 2 237, 2 239, 2 235.4 (in C₂Cl₄) and 2 241 cm⁻¹; ^r ref.^{5,7,8,10} give 1.35, 1.5, 1.29 and 0.82 (in C₂Cl₄) 10³ mol⁻¹ l cm⁻²; ^s ref.^{5,8,10,13} give 2 235, 2 235, 2 233 (in C₂Cl₄), and 2 235 cm⁻¹; ^t ref.^{5,7,8,10} give 3.98, 3.6, 3.08, and 3.55 (in C₂Cl₄) 10³ mol⁻¹ l cm⁻²; ^u compound 71 has been kindly presented to us by Prof. J. Kuthan, Prague; ^v cf. ref.⁴⁵; ^w ref.^{5,16} give frequencies 2 239 and 2 238 cm⁻¹, and intensities 0.92 and 1.11 10³ mol⁻¹ l cm⁻², resp.

with dilute sodium bisulphite solution, yield 0.85 g (59%), m.p. 182°C with decomposition (dilute ethanol). For C₁₀H₁₃IN₂ (288.1) calculated: 41.69% C, 4.55% H, 44.04% I, 9.72% N; found: 41.66% C, 4.53% H, 44.22% I, 9.90% N. 4-Cyanophenyl-trimethylammonium iodide (45) was prepared in the same way as the 3-isomer, only the quantity of benzene raised to 3 ml; yield 55%, m.p. 151°C (dilute ethanol). For C₁₀H₁₃IN₂ (288.1) calculated: 41.69% C, 4.55% H, 44.04% I, 9.72% N; found: 42.01% C, 4.32% H, 43.70% I, 9.34% N. In the literature²⁹ the melting point 181°C is given. 3,5-Diaminobenzonitrile (72). To a boiling solution of ferrous sulphate heptahydrate (40 g) in water 3,5-dinitrobenzonitrile³⁴ (1.93 g, 0.01 mol) and gradually concentrated ammonia (70 ml) was added, the solution was boiled 5 min and the precipitated Fe(OH)₃ filtered off. Crystals deposited from the filtrate upon cooling were collected and the mother liquor used to extract the Fe(OH)₃; this procedure was repeated once more. The last crop of the product was obtained by extraction of the last mother liquor with chloroform; total yield 0.66 g (50%), m.p. 194°C (water). For C₇H₇N₃ (133.2) calculated: 63.15% C, 5.30% H, 31.55% N; found: 62.98% C, 5.20% H, 31.22% N. 3,5-Bis(acetamido)benzonitrile (73). A solution of 3,5-diaminobenzonitrile (0.27 g, 0.002 mol) in acetic anhydride (2 ml), was refluxed 15 min, after cooling diluted with water, neutralized with K₂CO₃ and the product collected, yield 0.35 g (81%), m.p.

299°C (very dilute ethanol). For $C_{11}H_{11}N_3O_2$ (217.2) calculated: 60.82% C, 5.10% H, 19.35% N; found: 60.44% C, 5.39% H, 19.60% N. 3,5-Dichlorobenzonitrile (75). A suspension of 3,5-dichloro-4-aminobenzonitrile (1.87 g, 0.01 mol) in the mixture of H_3PO_4 (50 ml) and water (5 ml) was diazotized by solid sodium nitrite (0.75 g, 108%) at the temperature below 3°C during 20 min. 50% H_3PO_2 (10 ml) was added and the mixture left overnight at 0°C. Next day the product was collected, washed with $KHCO_3$ and purified by steam distillation from a slightly alkaline solution, yield 1.30 g (76%), m.p. 66°C (dilute ethanol). Ref.⁴⁹ gives m.p. 65°C for the product prepared from 3,5-dichloroaniline. 3,5-Dibromobenzonitrile (76) was prepared from 3,5-dibromo-4-aminobenzonitrile³⁹ by the same procedure, yield 78%, m.p. 97°C (dilute ethanol). Ref.⁵⁰ gives the same melting point for the product prepared in another way. 3,5-Dichloro-4-aminobenzonitrile (86) was prepared in the same way as described for the corresponding dibromo derivative³⁹; yield 87%, m.p. 120°C (dilute ethanol). In the patent literature⁵¹ the melting point 118°C is listed.

Spectral Measurements

The infrared absorption spectra were scanned in the region 2100–2300 cm^{-1} on a UR-10 instrument (Zeiss, Jena) with an LiF prism, and spectral slit width 2 cm^{-1} , using 0.01–0.1 cm cells. Concentration of the chloroform solution was 0.1–0.3 M. Less soluble compounds were measured in a saturated solution or in Nujol mull (Table I), in these cases intensities were not evaluated. The frequencies were read off to 0.1 cm^{-1} but their reproducibility was about ± 0.5 cm^{-1} , with sparingly soluble compounds and with asymmetric bands still less. The calibration was carried out directly on the basis of benzonitrile for which the value of 2230.5 cm^{-1} was chosen as the average of three most reliable literature data^{5,8,12}. The integrated absorption intensities were obtained by redrawing the absorption curve in the coordinates $\log(I_0/I)$ vs ν and integration of the area between the limits ν_1 and ν_2 . Since the absorption band was mostly the single one in a broad region, the values of ν_1 and ν_2 could be obtained graphically by drawing the base line of the spectrum, corresponding to 100% transmission. Usual range $\nu_2 - \nu_1$ was 80 cm^{-1} . Values obtained in this way have not been further corrected.

Experimental results are listed in Table I, and are generally in good agreement with literature data; for some typical compounds, detailed comparisons are given in footnotes to Table I. As far as the frequencies are concerned, the main differences arise from inconsistencies in calibration. Our figures agree with those of Sensi and Gallo⁵ to within the experimental error, the difference in calibration being 0.3 cm^{-1} and the mean deviation, after correcting for this difference, 0.7 cm^{-1} . Agreement with the data of Cabana and coworkers¹⁰ is also good in spite of a solvent change, the corresponding values being -0.1 and 1.2 cm^{-1} , respectively. Compared with the data of Thompson^{8,9}, or especially of Schiemenz¹³, the difference in calibration is significant (*viz.* -1.4 and 3.0 cm^{-1} , respectively). Other sets of data^{6,12,16} are too restricted for a significant comparison to be realised.

Comparison of intensities is more difficult, since apart from differing units there is a principal problem of different procedures used by individual authors. On average the data of Brown⁷ and of Thompson^{8,9} are some 5% higher than ours, whilst data of Sensi, Gallo⁵ are some 14% higher. These sets and ours essentially agree as to the relative values, the mean deviation being of the order of 10%. The data of Cabana¹⁰ obtained by a fundamentally different procedure are only 2% lower than ours. The remaining sets of data^{6,13,14,16} are again too small for a meaningful comparison, although those of Katritzky¹⁶ seem to be definitely higher than the others. We conclude that results from various laboratories must not be combined², and this is still more important with intensities than with frequencies.

DISCUSSION

From the total thirty-three fundamental vibrational modes of benzonitrile only the three a_2 out-of-plane modes are forbidden in the infrared^{11,52}. The situation is not changed by monoatomic or by symmetrical *para*-substituents, preserving the C_{2v} symmetry of the whole molecule. With unsymmetrical *para*-substituents and all *meta*-substituents the symmetry is lowered to C_s and all vibrational modes are allowed. Most of the frequencies have been observed and assigned¹¹. From the three characteristic bands of the CN group two lie below 400 cm^{-1} and have been little studied^{11,52}, the highly characteristic $C\equiv N$ stretching vibration being given most attention. Its frequency reflects essentially the changes of the $C\equiv N$ force constant, since that of the neighbouring $C-C$ bond varies in a parallel manner⁵³. Several correlations with σ constants^{9,13,15,54}, although limited to a relatively small number of compounds, confirmed that the $C\equiv N$ frequency is controlled mainly by polar substituent effects.

Our experimental frequencies are plotted *vs* the $\sigma_{m,p}$ constants in Fig. 1. Three different types of substituent effects can be distinguished:

1) *para*-Substituents without a free electron pair in the α -position control the frequency according to their constants σ_p and determine a straight line with slope $\rho = 7.61\text{ cm}^{-1}$. This value differs somewhat from literature data^{13,56} *viz.* 9.28 and 8.4 cm^{-1} , in the same solvent, or 5.58 , 5.3 and 6.7 cm^{-1} , respectively, in tetrachloromethane^{13,54,56}. However, these values were computed either for all substituents^{54,56} using constants⁵⁵ σ^+ , or for substituents¹³ with $\sigma > 0$. Fig. 1 shows conclusively that a division of substituents into groups is quite necessary. Within the group of

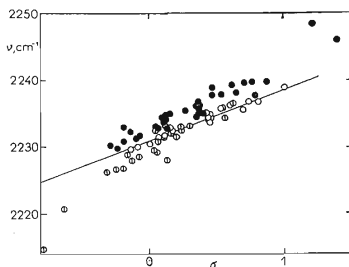


FIG. 1

Hammett Plot of the $C\equiv N$ Stretching Frequency (in CHCl_3) in Substituted Benzonitriles

○ *para*-Substituents without an alpha free electron pair, ⊙ other *para*-substituents, ● *meta*-substituents including 3,4- and 3,5-disubstitution.

para-substituents without a free electron pair the correlation is satisfactory according to the correlation coefficient $r = 0.973$, particularly when the uncertainty in some σ constants (Table I) is taken into account. The standard deviation from the regression line, $s = 0.53 \text{ cm}^{-1}$, is comparable to the supposed experimental error. According to our previous deduction³, the substituents act mainly by their inductive effect. A positive ρ constant means that the multiplicity of the $\text{C}\equiv\text{N}$ bond, and hence its force constant, are enhanced by electron withdrawing¹⁵; this behaviour is to be expected for all polar bonds whose positive end is oriented towards the substituent¹.

2) *para*-Substituent with a free electron pair in the α -position, including those with π -electrons, are strongly conjugated not only with the benzene nucleus but also directly with the cyano group. Hence they lower strongly the $\text{C}\equiv\text{N}$ frequency and the corresponding points are situated below the line defined by the first group of substituent. The enhanced conjugation may be expressed by the σ_p^+ constants⁵⁵ which are more negative than σ_p for donors while they are identical for acceptors. Correlations with σ^+ have been used several times for $\text{C}\equiv\text{N}$ frequencies^{54,56}. However, it follows from our data that this correction is rather a qualitative one. While it is adequate or still insufficient for strong donors ($\text{N}(\text{CH}_3)_2$), it is definitely too large for CH_3 and CH_2X groups. A more exact decision is prevented since many values of σ_p^+ are only approximate or not known at all. When the nine donor substituents, whose σ_p^+ are relatively dependable, are added to the previous set of twenty-three, the correlation with σ_p^+ yields $\rho 7.39 \text{ cm}^{-1}$, $r 0.972$, $s 1.08 \text{ cm}^{-1}$. (For CH_3 and halogens the appropriate σ_p^+ were used, but for CH_2X groups the σ_p were retained although σ_p^+ may somewhat differ). Although the correlation coefficient has not been changed, the standard deviation from the regression line is significantly higher (at $\alpha 0.005$) and exceeds already the experimental error. Part of the overall scatter could be also due to solvent effects — similarly as in the case of benzoic acids¹ — since the σ constants have been mostly determined in water. However, chloroform is a relatively polar solvent so that solvent effects seem not to be important in comparison with other effects involved. At any rate Fig. 1 shows that mesomeric effects affect strongly the force constant and stretching frequency of the $\text{C}\equiv\text{N}$ bond; their participation when compared to inductive effects is much larger than in chemical reactivity of benzoic acids, which served to derive σ_p constants.

3) All the *meta*-derivatives show unique behaviour, their frequency being higher than would correspond to their electronic effects as expressed by the constant σ_m . We have called this phenomenon the *meta*-effect²; it is specific for the infrared spectroscopy, particularly for stretching frequencies. In previous correlations^{9,13,15,54,56} this effect has been not detected due to small number of *meta*-derivatives studied; however, Fig. 1 yields a convincing proof. The raising of frequency amounts most often to $1-4 \text{ cm}^{-1}$ and neither depends upon electronic effects of the substituent, nor its size, nor its mass. As previously², we have no definite

explanation of this behaviour. It cannot be accounted for by a correlation with inductive and mesomeric constants in any ratio, since it is observed with substituents of quite different type.

We suspected initially distortion of symmetry in the *meta*-derivatives to be the possible source. Hence we investigated several 3,5-bis-derivatives in which the C_{2v} symmetry is restored (Table I, 70–76). However, the *meta*-effect is encountered with all these compounds, approximately with doubled intensity when compared to the corresponding mono-substituted derivatives. A tentative hypothesis was advanced² that this effect could possibly be connected with C—H vibrations since an isolated hydrogen atom between two substituents is a common feature of all *meta*-derivatives. This idea is not supported by the frequency of 3-cyanopyridine (Table I 88), since, exceptionally, the aza substituent does not show any *meta*-effect. The behaviour of the 3,4-bisderivatives (Table I 77, 79–85), is also remarkable. When the effect of the 4-substituents, computed from the appropriate monoderivative, is subtracted from their $C\equiv N$ frequency, the resulting effect of the 3-substituent is normal, corresponding to the σ_m constant. A *para*-substituent is thus able to cancel the *meta*-effect completely. This is not true for the 3,4,5-tris-derivatives (86 and 87) but their number is too small for more definite conclusion to be drawn.

Hence we believe that the *meta*-effect is connected with kinematic rather than with electronic phenomena and that it is encountered only in vibrational spectra. For the time being it is not possible to limit precisely its range of validity. It seemed to be associated with the vibrations of bonds adjacent to the benzene nucleus², however, it is absent in the C=O frequency of monomeric and dimeric benzoic acids⁵⁷; possibly the symmetry also plays some role. At any rate the *meta*-effect essentially prevents the proposed determination⁵⁴ of new σ constants from spectroscopic data and also makes impossible the direct comparison of IR frequencies of *meta* and *para*-derivatives according to equation (2) as is possible with reactivity data³. *E.g.* the plot

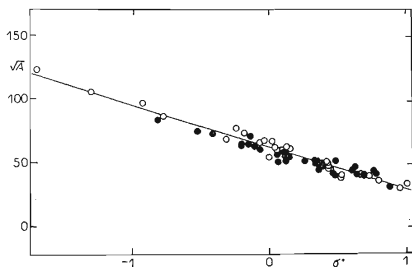


FIG. 2

Hammett Plot of \sqrt{A} (in CHCl_3) of the $\text{C}\equiv\text{N}$ Stretching Vibration in Substituted Benzonitriles
 ○ *para*-Substituents, ● *meta*-substituents including 3,4- and 3,5-derivatives.

of ν_p vs ν_m from Table I would reveal only the *meta*-effect and would not permit determination of the slope λ .

The intensity of the C \equiv N stretching mode is rather low and at the same time relatively sensitive to substitution. This has been explained in terms of two opposing forces, resulting from bond stretching, *viz.* charge separation and rehybridization¹⁰. The sensitivity to substitution has been employed in many correlations with substituents constants^{7,9,54,58-60} and the results differed according to the function of the integrated intensity A used in the plot, the type of σ constant, and selection of data. As previously² we prefer plotting of \sqrt{A} which is theoretically sound⁵⁹. When our values are plotted against substituents constants, the best correlation is obtained with σ^+ (Fig. 2). These constants have already been preferred by Brown⁵⁹ and Juchnovski⁵⁸, while Rao and Venkataraghavan⁵⁴ obtained a better correlation with the common σ constants. This last result demonstrates, in our opinion, the danger of drawing conclusions from restricted sets of data.

There is no trace of any *meta*-effect in Fig. 2, substituents of all types lying near a single regression line. With r 0.984 the correlation is very satisfactory; the standard deviation from the regression line $s = 3.16 \text{ mol}^{-1/2} \text{ l}^{1/2} \text{ cm}^{-1}$ represents at worst a 20% accuracy (at A 1000) or 7% at best (at A 9000). The former value exceeds the supposed mean experimental error, however, measurements can be quite difficult for particular compounds and their accuracy varies. The constant $\rho = -32.5 \text{ mol}^{-1/2} \text{ l}^{1/2} \text{ cm}^{-1}$ is close to that read off from Brown's diagram⁵⁹.

The meaning of ρ in intensity correlations has been seldom discussed and is not fully understood, particularly in connection with ρ for the corresponding frequency correlation. Katritzky and Ambler⁶¹ reasoned that the change in the dipole moment determining the intensity is the greater, the larger is the moment itself (also^{54,62}). Hence the stretching band intensities of multiple bonds conjugated with the benzene nucleus are increased by donors when the bond dipole is oriented with the positive end towards the substituent. This is the case for substituted nitriles. Application of the same principle to the stretching of single bonds and to inductive substituent effects is also possible; however, the expected effect is much less. In this way the necessity to use

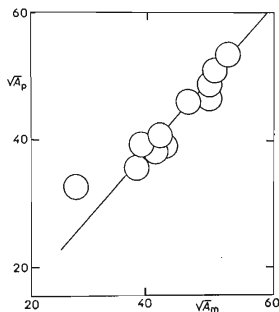


FIG. 3
Plot of \sqrt{A} of the C \equiv N Stretching Vibration *para*-
vs meta-Derivatives According to Equation (2)
The line has the theoretical slope 1.14.

σ^+ constants is substantiated. A consequent application of the principle in connection with the foregoing discussion of frequency correlations would lead to the prediction that the signs of ρ 's in corresponding frequency and intensity correlations are always opposite. This is not generally true^{9,60,63}, but the exceptions concern mostly bands corresponding to complex motions. A more fundamental theoretical approach would be thus desirable.

Since no *meta*-effect is exhibited with $C\equiv N$ intensities, these can serve to confirm the relation³ (2), written for intensities instead for frequencies. In Fig. 3 the values of \sqrt{A} are plotted for hydrogen and ten acceptor groups without a free electron pair, the CH_2X groups being excluded since the functional group acts as a strong acceptor. The line drawn through the point H with slope 1.14 confirms that equation (2) is fulfilled with the exception, as yet unexplained, of the substituent SO_2Cl . The precision of the data is not sufficient to check the value of the coefficient λ , or to draw any additional conclusions.

To conclude we believe that intensities of IR bands are important physical quantities for understanding substituent effects and are more suitable for correlation with reactivity parameters than frequencies. The importance of the latter has been overestimated in our opinion. Hence the two spectroscopic quantities are controlled by different factors even in simple model compounds. The intensities are particularly valuable for studying mesomeric effects which play an important role as manifested in the use of σ^+ constants. However, the insufficient accuracy and many practical difficulties prevent a broader use of intensity measurements at present.

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