

**SUBSTITUENT EFFECTS IN INFRARED SPECTROSCOPY. II.\***  
**CHARACTERISTIC FREQUENCIES OF THE NITRO GROUP**  
**IN *meta*- AND *para*-SUBSTITUTED NITROBENZENES**

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Received May 26th, 1971

Infrared absorption spectra of ninety five *meta*- and *para*-substituted nitrobenzenes have been recorded in chloroform solution and in Nujol mull in the region 650–1600 cm<sup>-1</sup>. The anti-symmetrical stretching frequencies of *para* derivatives correlate with  $\sigma_p$  constants while those of *meta* derivatives are enhanced by all substituents, irrespective of their mass or electronic character (the *meta* effect). Very little correlation with  $\sigma$  values but a distinct *meta* effect has been found with the symmetrical stretching frequencies. The absorption band at 703 cm<sup>-1</sup> presents a unique dependence on substitution, supporting its assignment to a  $b_2$  ring deformation mode rather than to the NO<sub>2</sub> group. All the relationships are merely statistical in character, one reason for the deviations may be coupling with aromatic ring vibrations. No regularity has been detected for the intensities of  $\nu_{as}$  and  $\nu_s$  vibrations.

In the first communication of this series we discussed in general the possibility of analysing substituent effects on infrared frequencies and their relation to reactivity parameters<sup>1</sup>. The main suppositions for such studies are a) a sufficient number of derivatives in a series, including substituents of different types, b) the choice of an appropriate vibration, little dependent on mass and combination effects, and c) the possibility of carrying out the measurements with a sufficient accuracy in relation to the substituent effect.

Benzene *meta* and *para* derivatives are an advantageous system with respect to preparative possibilities, i.e. the number of derivatives, and little influence of the effects sub b). The latter is due to the distance of the substituent and the position of the active bond on the periphery of the molecule<sup>2</sup>. On the other hand this distance inevitably reduces the sensitivity to substitution<sup>3,4</sup>, so that the problem of accurate measurement becomes critical. A further advantage of benzene *meta* and *para* derivatives is the possibility of correlating the data by the Hammett equation (1) and by equation (2) derived by us previously<sup>5</sup> for substituents without a lone electron pair in the  $\alpha$ -position. For infrared frequencies these equations take the forms:

$$\nu = \nu^0 + \rho\sigma_{m,p}, \quad \nu_p - \nu^0 = \lambda(\nu_m - \nu^0). \quad (1, 2)$$

\* Part I: This Journal 36, 534 (1971).

While the constant  $\rho$  ( $\text{cm}^{-1}$ ) must be determined for each reaction series, the dimensionless constant  $\lambda$  is universal<sup>5</sup> and equal to 1.14. Both equations belong to the best supported empirical relationships, hence significant conclusions can be drawn from observed deviations.

In this paper we are dealing with characteristic frequencies of the nitro group, particularly the symmetrical ( $\nu_s$ ) and antisymmetrical ( $\nu_{as}$ ) stretching frequencies and the frequencies in the 700–900  $\text{cm}^{-1}$  region, which have not yet been unambiguously assigned<sup>6–14</sup>. Aromatic nitro compounds are favourable due to their preparative accessibility and good solubility; for that reason a number of experimental studies have been devoted to them using the infrared<sup>6–9,13–23</sup> as well as Raman<sup>14,24,25</sup> spectroscopy. For our purposes the main shortcoming of all these studies was the insufficient number and unsystematic choice of substituents, particularly *meta* substituents and electron acceptor groups were usually little represented. A disadvantage of nitro compounds is the relatively low attainable accuracy, which is, however, in the case of certain frequencies (*e.g.* the one at 703  $\text{cm}^{-1}$ ) counterbalanced by their sensitivity to substitution. The sensitivity of the  $\nu_{as}$  and especially  $\nu_s$  frequency is considerably less and the general trend can be masked by experimental errors. The only way out is to study a great number of derivatives, giving the results a merely statistical character. In addition to frequencies we measured the intensities of the symmetrical and antisymmetrical stretching vibrations. These were less studied previously<sup>17,24,25</sup>; instead of absolute values, their ratio was also recommended as a suitable parameter<sup>26</sup>. In order to maintain comparable conditions for as many compounds as possible, we chose chloroform solution for stretching vibrations; the bands in the 600–900  $\text{cm}^{-1}$  region, less solvent dependent, could be followed in Nujol mull.

## EXPERIMENTAL AND RESULTS

All the *meta*- and *para*-substituted nitrobenzenes 1–95 are known compounds, they were obtained either by purifying commercial products, or prepared according to the literature. The pertinent references<sup>27–29</sup> are given only for some less common compounds, see the footnotes to Table I. The physical constants agreed with literature.

The infrared absorption spectra in the region 650–1600  $\text{cm}^{-1}$  were scanned in the  $4 \cdot 10^{-2}$  M chloroform solution (dried on a silicagel column) and using the Nujol technique. The instrument Unicam SP 100 with a double monochromator prism-grating was calibrated with polystyrene. The frequencies were read to  $\pm 0.5 \text{ cm}^{-1}$ . The integrated absorption intensities  $A$  were calculated from the apparent molar absorptivity  $\epsilon^a$  and the half-intensity width  $\Delta\nu_{1/2}$  according to  $A = 2.303 (\pi/2) \Delta\nu_{1/2} \epsilon^a$ . The experimental results are listed in Table I. The agreement between our data and those of previous workers<sup>15,17,18,21</sup> using the same solvent, is not fully satisfactory. We have compared the symmetrical and antisymmetrical stretching frequencies of nine selected compounds, which had been measured several times, with the following results. Our figures are very close to those of Conduit<sup>17</sup> except for the antisymmetrical frequency of 1,4-dinitrobenzene; omitting this compound there is a difference in calibration of c. 1.5  $\text{cm}^{-1}$  and after correcting for this difference a scatter of c. 1.5  $\text{cm}^{-1}$ . Our data also agree with those of Brown<sup>15</sup> as far as the antisymmetrical frequency is concerned and with Katritzky–Simmons<sup>18</sup> and Yates–Thompson<sup>21</sup> as to the symmetrical one. However, the distance between the two frequencies is given by

TABLE I  
 Infrared Spectral Data of 3- and 4-Substituted Nitrobenzenes

No	Substituent	CHCl <sub>3</sub>					Nujol		
		$\nu_s$ cm <sup>-1</sup>	$A_s^a$	$\nu_{as}$ cm <sup>-1</sup>	$A_{as}^a$	$\delta$ cm <sup>-1</sup>	$\nu_s$ cm <sup>-1</sup>	$\nu_{as}$ cm <sup>-1</sup>	$\gamma$ cm <sup>-1</sup>
1	H	1 348	2.11	1 530.5	3.20	858	1 344	1 535	703
2	3-CH <sub>3</sub>	1 349.5	1.93	1 531	2.88	870	1 348	1 536	728
3	4-CH <sub>3</sub>	1 345	2.37	1 524.5	2.50	862	1 343	1 527	734
4	4-C(CH <sub>3</sub> ) <sub>3</sub>	1 347	2.70	1 527	2.28	862	1 345	1 531	754.5
5	4-CH <sub>2</sub> COOH	1 348	2.71	1 526	2.91	858	1 344	1 524	750
6	3-CH <sub>2</sub> OH	1 350	1.74	1 535	1.98	—	1 352	1 531	729.5
7	4-CH <sub>2</sub> OH	1 345	2.87	1 525	2.63	862	1 341	1 509	733.5
8	3-CH <sub>2</sub> Cl	1 350.5	1.79	1 533	2.52	814	1 349	1 524	740
9	4-CH <sub>2</sub> Cl	1 348	2.34	1 527.5	2.91	863	1 345	1 533	756
10	3-CH <sub>2</sub> Br	1 350	2.27	1 536	2.84	880	1 349	1 539	735
11	4-CH <sub>2</sub> Br	1 347	2.47	1 527	3.01	864	1 346	1 541	750
12	3-CH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> <sup>b</sup>	1 347	3.99	1 535	3.64	887	1 346	1 540	737
13	4-CH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> <sup>b</sup>	1 348	3.35	1 528	2.85	877	—	—	—
14	4-CHBr <sub>2</sub>	1 347.5	2.53	1 531	2.81	860	1 341	1 534	719
15	3-C <sub>6</sub> H <sub>5</sub>	1 351	2.39	1 533.5	2.85	854	1 348	1 537	771
16	4-C <sub>6</sub> H <sub>5</sub>	1 345	3.68	1 521.5	2.37	860	1 343	1 516	738
17	4-CH=CHC <sub>6</sub> H <sub>5</sub>	1 342	4.78	1 522.5	2.84	872	1 342	1 514	765
18	3-CH=CHCOC <sub>6</sub> H <sub>5</sub>	1 352	2.50	1 536	3.18	865	1 350	1 530	733
19	4-CH=CHCOC <sub>6</sub> H <sub>5</sub>	1 345	3.46	1 525.5	2.83	859	1 343	1 535	743
20	3-CH=CHCOOH	—	—	—	—	—	1 362	1 524	742
21	4-CH=CHCOOH	—	—	—	—	—	1 341 <sup>c</sup>	1 531 <sup>c</sup>	756
22	3-CH=NOH	1 361	2.26	1 536.5	3.20	836	1 350	1 539.5	732
23	4-CH=NOH	1 345.5	2.48	1 526	2.75	853	1 347.5	1 539.5	746
24	3-CHO	1 351	1.88	1 543	2.05	827	1 350	1 538	728
25	4-CHO	1 344.5	2.09	1 539	2.50	852	1 342	1 542	737
26	3-COCH <sub>3</sub>	1 350	1.96	1 536	2.41	880	1 347	1 526	717
27	4-COCH <sub>3</sub>	1 344.5	2.08	1 534.5	2.89	857	1 342	1 528	744
28	4-COCH <sub>2</sub> Br	1 343.5	1.97	1 534	2.55	859	1 343	1 525	743
29	3-COC <sub>6</sub> H <sub>5</sub>	1 348	2.19	1 538	2.14	877	1 350	1 539	736
30	4-COC <sub>6</sub> H <sub>5</sub>	1 353	(2.48)	1 528	2.62	855	1 356	1 517	732
31	3-COCH=CHC <sub>6</sub> H <sub>5</sub>	1 349.5	2.02	1 536.5	2.47	869	1 347	1 527	739
32	4-COCH=CHC <sub>6</sub> H <sub>5</sub>	1 331.5	3.08	1 529.5	2.76	858	1 332	1 517	739
33	3-CONH <sub>2</sub>	—	—	—	—	—	1 349	1 523	717
34	4-CONH <sub>2</sub>	—	—	—	—	—	1 342	1 530.5	741
35	3-CON(CH <sub>3</sub> ) <sub>2</sub>	1 352	2.32	1 538	2.44	863	1 349	1 541	756
36	4-CON(CH <sub>3</sub> ) <sub>2</sub>	1 350.5	2.31	1 529	3.19	864	1 349	1 527	735.5
37	3-CON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1 351.5	2.35	1 540	2.65	851	1 349	1 534	722
38	4-CON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1 347.5	3.00	1 529.5	2.77	863	1 345	1 523	748.5
39	3-CONHNH <sub>2</sub>	—	—	—	—	—	1 337	1 535	723
40	4-CONHNH <sub>2</sub>	—	—	—	—	—	1 354	1 534	730

TABLE I  
(Continued)

No	Substituent	CHCl <sub>3</sub>					Nujol		
		$\nu_s$ cm <sup>-1</sup>	$A_s^a$	$\nu_{as}$ cm <sup>-1</sup>	$A_{as}^a$	$\delta$ cm <sup>-1</sup>	$\nu_s$ cm <sup>-1</sup>	$\nu_{as}$ cm <sup>-1</sup>	$\gamma$ cm <sup>-1</sup>
41	4-CONHOH	—	—	—	—	—	1 356	1 522	733
42	3-COOH	1 350.5	2.13	1 539	2.67	881	1 351	1 530	720
43	4-COOH	—	—	—	—	—	1 348	1 542	715
44	3-COOCH <sub>3</sub>	1 349.0	2.04	1 538	2.44	873	1 350	1 535 <sup>d</sup>	717
45	4-COOCH <sub>3</sub>	1 347.5	1.09	1 534	2.20	874	1 348	1 527	716
46	3-COOC <sub>2</sub> H <sub>5</sub>	1 351	1.91	1 536	2.45	868	1 350	1 539	719
47	4-COOC <sub>2</sub> H <sub>5</sub>	1 348	2.12	1 529.5	2.58	876	1 348	1 536	717
48	4-COOCH(CH <sub>3</sub> ) <sub>2</sub> <sup>e</sup>	1 348	(1.90)	1 531	2.79	875	1 344	1 522	716
49	3-COCl	1 350.5	2.64	1 541	2.73	880	1 352	1 535	720
50	4-COCl	—	—	—	—	—	1 349	1 543	714
51	3-CN	1 353	1.85	1 544	3.48	812	1 356	1 536 <sup>f</sup>	733
52	4-CN	1 343	1.89	1 534	2.53	862	1 346	1 528	745
53	3-NH <sub>2</sub>	1 352.5	2.03	1 534	4.06	870	1 346	1 523	733
54	4-NH <sub>2</sub>	1 334	4.97	1 508	3.25	842	1 334	1 503	751
55	3-N(CH <sub>3</sub> ) <sub>2</sub>	1 348	(3.89)	1 536	5.57	878	1 340	1 536 <sup>g</sup>	770
56	4-N(CH <sub>3</sub> ) <sub>2</sub>	1 318	—	1 527	2.05	833	1 327	1 530	749
57	3-NHCOCH <sub>3</sub>	—	—	—	—	—	1 349	1 533	740
58	4-NHCOCH <sub>3</sub>	—	—	—	—	—	1 345	1 507	747
59	3-NHCOC <sub>6</sub> H <sub>5</sub>	1 350	1.41	1 535	3.78	882	1 353	1 534	732
60	4-NHCOC <sub>6</sub> H <sub>5</sub>	—	—	—	—	—	1 342.5	1 530	745
61	3-NCS	—	—	—	—	—	1 347	1 540	731.5
62	4-NCS	1 342.5	4.13	1 527	3.04	855	1 340	1 530	743
63	4-NHNH <sub>2</sub>	—	—	—	—	—	1 335	1 533	749
64	3-N=NC <sub>6</sub> H <sub>5</sub>	1 353	2.13	1 536	2.94	854	1 353	1 526	736
65	4-N=NC <sub>6</sub> H <sub>5</sub>	1 345	3.41	1 527	2.92	862	1 342	1 502	747
66	4-NHSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	1 344	4.89	1 528	2.98	867	1 343	1 526 <sup>h</sup>	748
67	3-NO <sub>2</sub>	1 346	1.67 <sup>i</sup>	1 543	2.15 <sup>i</sup>	837	1 346	1 545	710
68	4-NO <sub>2</sub>	1 338	1.68 <sup>i</sup>	1 556	2.34 <sup>i</sup>	841	1 345	1 560	707
69	3-OH	1 350	2.58	1 531	(4.1)	880	1 349	1 528	740
70	4-OH	1 336.5	4.61	1 521.5	2.58	866	1 343	1 518	753
71	3-OCH <sub>3</sub>	1 350	2.78	1 535	5.01	864	—	—	—
72	4-OCH <sub>3</sub>	1 342	(4.18)	1 518	(3.39)	852	1 341	1 524	751.5
73	3-OCOCH <sub>3</sub>	1 350	2.04	1 537.5	3.47	862	1 352	1 535	734
74	4-OCOCH <sub>3</sub>	1 347	2.50	1 530.5	2.54	867	1 342	1 522.5	748
75	3-OCOC <sub>6</sub> H <sub>5</sub>	—	—	—	—	—	1 351	1 536	732
76	4-OCOC <sub>6</sub> H <sub>5</sub>	1 347	2.02	1 531	2.31	864	1 344	1 524	745
77	4-OSO <sub>2</sub> CH <sub>3</sub> <sup>j</sup>	1 349	1.51	1 532.5	2.63	876	1 344	1 527	748
78	3-OSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	1 356	(3.02)	1 539	3.79	836	1 357	1 532	733
79	4-OSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	1 347	4.35	1 533.5	2.57	846	1 348	1 528	737.5
80	4-S-C <sub>6</sub> H <sub>5</sub>	1 338.5	4.29	1 521	(2.18)	847	1 336	1 525	745

TABLE I  
 (Continued)

No	Substituent	CHCl <sub>3</sub>					Nujol		
		$\nu_s$ cm <sup>-1</sup>	$A_s^a$	$\nu_{as}$ cm <sup>-1</sup>	$A_{as}^a$	$\delta$ cm <sup>-1</sup>	$\nu_s$ cm <sup>-1</sup>	$\nu_{as}$ cm <sup>-1</sup>	$\gamma$ cm <sup>-1</sup>
81	3-SCN	—	—	—	—	—	1 348	1 534	740.5
82	3-SO <sub>2</sub> CH <sub>3</sub>	1 348.5	2.26	1 538	2.63	878	1 354	1 529	728
83	4-SO <sub>2</sub> CH <sub>3</sub>	1 346	(1.85)	1 538	2.61	860	1 347	1 534	732
84	3-SO <sub>2</sub> NH <sub>2</sub>	—	—	—	—	—	1 350	1 533	735
85	4-SO <sub>2</sub> NH <sub>2</sub>	—	—	—	—	—	1 349	1 524	740
86	3-SO <sub>2</sub> Cl	1 350	1.68	1 542	2.36	878	1 350	1 533	732
87	4-SO <sub>2</sub> Cl	1 345.5	1.81	1 541	2.74	857	1 342	1 533	736
88	3-F	1 353	1.75	1 538.5	3.82	885	1 350.5	1 543	733
89	4-F	1 348	2.30	1 532	2.61	868	—	—	—
90	3-Cl	1 350	2.30	1 546	2.52	880	1 345	1 543	728
91	4-Cl	1 343.5	2.22	1 528	2.41	856	1 340	1 529	738
92	3-Br	1 347	2.33	1 536.5	3.75	874	1 344.5	1 540	728.5
93	4-Br	1 343	(2.32)	1 527.5	3.05	855	1 343	1 535	735
94	3-I	1 345.5	2.75	1 534.5	3.26	869	1 344	1 537	726
95	4-I	1 348.5	(2.37)	1 528.5	2.57	852	1 340	1 533	731

<sup>a</sup> Integrated absorption intensity.  $10^4$  l mol<sup>-1</sup> cm<sup>-2</sup>; <sup>b</sup> prepared acc. to ref.<sup>27</sup>; additional bands at: <sup>c</sup> 1 349 and 1 538 cm<sup>-1</sup>; <sup>d</sup> 1 530 cm<sup>-1</sup>. <sup>e</sup> cf. ref.<sup>28</sup>; <sup>f</sup> 1 541 cm<sup>-1</sup>; <sup>g</sup> 1 526 cm<sup>-1</sup>; <sup>h</sup> 1 524 cm<sup>-1</sup>. <sup>i</sup> Per one nitro group; <sup>j</sup> cf. ref.<sup>29</sup>.

these authors<sup>15,18,21</sup> as in the average 5, 4 and 7 cm<sup>-1</sup>, respectively, less than by us or Conduit<sup>17</sup>. In addition some discrepancies up to 20 cm<sup>-1</sup> are encountered, which cannot be understood, e.g. the antisymmetrical vibrations of 4-nitrophenol and 4-nitroanisole<sup>21</sup>. The conclusion is that results from various laboratories must not be combined in one correlation.

## DISCUSSION

The idealized four-atom molecule XNO<sub>2</sub> of C<sub>2</sub> symmetry has six fundamental vibrational modes. The NO<sub>2</sub> symmetrical stretching ( $\nu_s$ ), the C—N stretching ( $\nu_{CN}$ ) and the NO<sub>2</sub> symmetrical (scissoring) deformation ( $\delta$ ) modes belong to the a<sub>1</sub> species, the out-of-plane bending<sup>11</sup> or wagging<sup>14</sup> mode ( $\gamma$ ) is a b<sub>1</sub> species and the NO<sub>2</sub> antisymmetrical stretching vibration ( $\nu_{as}$ ) and NO<sub>2</sub> in-plane rocking ( $r$ ) modes belong to the b<sub>2</sub> species.

All the frequencies were tentatively assigned in the case of nitromethane<sup>15,30</sup>. In the spectrum of nitrobenzene, there is in addition the a<sub>2</sub> torsional mode ( $t$ ), not found experimentally<sup>10,14</sup>, and twenty-nine further modes connected with vibrations of the phenyl group. Hence the assignment

is more difficult and is still a subject of controversy, except the vibrations  $\nu_s$  and  $\nu_{as}$  assigned already by Randle and Whiffen<sup>6</sup> to intense bands at 1348 and 1530  $\text{cm}^{-1}$ , respectively. For the remaining bands the spectra of nitrobenzene-[<sup>18</sup>O] and -[<sup>18</sup>O<sub>2</sub>] seem to be decisive, leading to the assignment<sup>11</sup> of the 417  $\text{cm}^{-1}$  band to  $r$ , 532  $\text{cm}^{-1}$  to  $\gamma$ , 850  $\text{cm}^{-1}$  to  $\delta$  and 1109  $\text{cm}^{-1}$  probably to  $\nu_{\text{CN}}$ . Alternatively the 850  $\text{cm}^{-1}$  band was assigned<sup>6,13</sup> to  $\nu_{\text{CN}}$  (or at least should involve the C—N stretching<sup>10</sup>), the 682  $\text{cm}^{-1}$  band<sup>8,10</sup> to  $\delta$  (or having a contribution<sup>12,14</sup> from  $\delta$ ), the 704  $\text{cm}^{-1}$  band<sup>9</sup> to  $\gamma$  (or with a contribution<sup>14</sup> of  $\gamma_{\text{CH}}$  mode) and 532  $\text{cm}^{-1}$  band<sup>9,14</sup> to  $r$ .

The situation is still more complicated with derivatives of nitrobenzene<sup>14</sup> since various frequencies are shifted in a different way by substitution. On the other hand shifts can be of diagnostic help in assignment. For these reasons we discuss first the  $\nu_{as}$  and  $\nu_s$  frequencies.

The NO<sub>2</sub> antisymmetrical stretching band is rather sensitive to substitution<sup>18</sup> and — in the case of *meta* and *para* substituents — determined by their polar properties. This follows from the correlations with reactivity constants, reported several times. Either common constants<sup>3,15,22,23</sup>  $\sigma$ , or constants  $\sigma^+$  or  $\sigma^-$ , expressing the enhanced activity of substituents as donors<sup>3,19,21</sup> or acceptors<sup>7</sup>, respectively, were used. According to the kind of constants used the slope  $\rho$  in Eq. (1) was from 19 to 30  $\text{cm}^{-1}$ ; a single report that no correlation exists<sup>20</sup> may be due to the KBr technique employed. Our experimental data (in solution) have been plotted against the common  $\sigma$  constants<sup>31</sup> in Fig. 1. Many values of  $\sigma$  had to be estimated<sup>31</sup> and several points deviate badly from the over-all dependence, e.g. those for the substituents\* 4-N(CH<sub>3</sub>)<sub>2</sub> and 4-NO<sub>2</sub>. However, due to the great number of points, the statistical weight of the conclusions is not affected. A relatively rough correlation of  $\nu_{as}$  of *para* derivatives

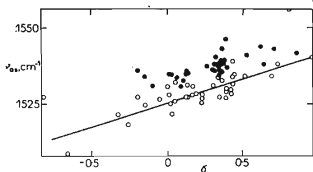


FIG. 1

Hammett Plot of the NO<sub>2</sub> Antisymmetrical Stretching Frequency (in CHCl<sub>3</sub>) vs  $\sigma_{m,p}$  Constants

Derivatives:  $\circ$  *para*,  $\bullet$  *meta*, the regression line has been computed for *para* derivatives except NO<sub>2</sub> and N(CH<sub>3</sub>)<sub>2</sub>.

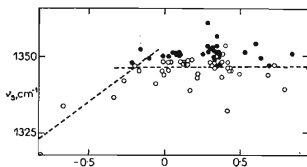


FIG. 2

Hammett Plot of the NO<sub>2</sub> Symmetrical Stretching Frequency (in CHCl<sub>3</sub>)

Derivatives:  $\circ$  *para*,  $\bullet$  *meta*, the lines are only estimated.

\* The raised  $\nu_{as}$  and depressed  $\nu_s$  frequencies of 1,4-dinitrobenzene are paralleled by similar behaviour of the terephthalate anion<sup>34</sup>.

with  $\sigma_p$  constants appears with  $\rho$  16 cm<sup>-1</sup>; even when the substituents 4-NO<sub>2</sub> and 4-N(CH<sub>3</sub>)<sub>2</sub> are omitted. The fit is very poor according to the correlation coefficient ( $r$  0.8320) but acceptable according to the standard deviation ( $s$  3.33 cm<sup>-1</sup>); this is due to the low absolute value of  $\rho$ . There is evidently no reason to use  $\sigma_p^-$  constants, while a definite decision between  $\sigma_p$  and  $\sigma_p^+$  cannot be made; this is because the standard deviations are not significantly different (even at the confidence level  $\alpha$  0.25) and several values of  $\sigma_p^+$  are lacking.

In addition our data reveal a special effect which has not been reported by previous investigators<sup>7,15,19-21</sup> due to the small number of *meta* derivatives in their series: All the *meta* derivatives have enhanced frequencies with respect to the *para* line by some 5–10 cm<sup>-1</sup>, any dependence of this deviation on the substituent, *e.g.* on its mass, cannot be detected. At any rate, when *para* and *meta* derivatives are combined into one set, the standard deviation rises to 4.92 cm<sup>-1</sup>, *i.e.* significantly at  $\alpha = c$ . 0.006. We shall refer to this phenomenon, observed already with substituted benzonitriles<sup>32</sup>, as the *meta* effect and we believe that it is characteristic for vibrational frequencies. It cannot be due to any electronic effects of substituents, *e.g.* to changed proportions of their inductive and mesomeric parts, since it is observed with substituents of all kinds. Neither is it connected with a simple distortion of symmetry since it has been found with 3,5-bis-derivatives with a doubled intensity<sup>32</sup>. Nor can any simple explanation based on kinematic coupling be accepted; due to the distance between the N—O (or C≡N) and X—C bonds the pertinent non-diagonal force constant is equal to zero for the *meta* as well as for the *para* position<sup>33</sup>. A hypothesis which cannot be rejected for the time being, would suppose mixing with some C—H vibration common to all *meta* derivatives; of course, the final explanation will require further experiments.

From the phenomenological point of view, it seems that the *meta* effect is restricted to stretching vibrations of bonds next to the benzene nucleus. It is certainly not involved in the O—H stretching frequency of substituted benzoic acids<sup>1</sup> while the available data on the antisymmetrical stretching frequencies give some support to its presence in benzoate anions<sup>34,35</sup>, but not in benzenesulfinate anions<sup>36</sup>. In the latter case the mass or size of the sulfur atom may play some role. In the field of correlation equations (linear free energy relationships) the existence of the *meta*-effect represents a serious argument against the proposal<sup>2,3</sup> to determine new  $\sigma$  constants from infrared spectral data. Of course, equation (2) cannot be used for frequencies involving the *meta*-effect; *e.g.* the plot of  $\nu_{as-para}$  vs  $\nu_{as-meta}$  of the NO<sub>2</sub> group (not shown) would reveal only this effect and could not yield the value of  $\lambda$ .

A second point of general significance is the meaning of the proportionality constant  $\rho$ , defined in our case only by *para* substituents. Although discussion of the reaction constant  $\rho$  is one of the main purposes of correlation equations<sup>31</sup>, to our knowledge no completely satisfactory explanation of its significance has been done in the infrared spectroscopy. Our opinion<sup>1</sup>, that the natural polarity of the stretched

bond determines the sign of  $\rho$  seems to us more general than the classification based on the acceptor or donor character of the active group and restricted to the stretching of bonds adjacent to the benzene nucleus<sup>37</sup>. Our previous formulation<sup>1</sup> is in agreement with the present result, since the N—O dipole is oriented with its positive end towards the substituent, and  $\rho$  is positive.

However, with the antisymmetrical vibration the substituent effect on the O—N—O angle is certainly superposed to that on the force constant so that the resulting picture is more complex. The straightforward rule can probably be applied only to simple stretching vibrations.

The NO<sub>2</sub> symmetrical stretching band is believed to be less substituent dependent than the antisymmetrical one<sup>7,18</sup>, except in its sensitivity to steric hindrance<sup>16</sup>. Partial linear correlations with  $\sigma$  constants have been described, either with a break<sup>7,15</sup> approximately at  $\sigma = 0$  and practical independence on positive  $\sigma$  values, or split into two almost parallel lines<sup>25</sup>. Our experimental data plotted in Fig. 2 agree essentially with the former finding, although the left-hand straight line is based essentially on three points only. The use of  $\sigma^+$  constants would reduce the angle of the two branches but would not alter the whole pattern. An explanation was advanced<sup>7</sup> based on coupling with the  $\nu(\text{CN})$  mode so that the  $\nu_s$  frequency depends sensitively on the C—N force constant; however, the reason remains obscure why acceptor groups should affect the C—N relatively more than the N—O bond, when compared with donor groups. In our opinion the interplay of inductive and mesomeric effects could be of importance; the former, prevailing in substituents with positive  $\sigma$ , influences more the nearer C—N bond.

In addition to the pattern described, Fig. 2 reveals a clear *meta* effect, notwithstanding some unexplained deviations and the overall large scatter. This confirms the generality of this phenomenon when stretching of bonds next to the benzene nucleus is involved.

The difference  $\nu_{\text{as}} - \nu_s$  might also serve as an appropriate measure of substituent effects, since the *meta* effect and certain irregularities could be eliminated. However, Fig. 3 reveals that it is not the case. Even when the *meta* effect is almost compensated, the fit is poor, in particular the deviations of the 4-NO<sub>2</sub> and 4-N(CH<sub>3</sub>)<sub>2</sub> substituent have been doubled instead of compensated. It follows that, from the empirical point of view, the difference  $\nu_{\text{as}} - \nu_s$  cannot be recommended as a useful parameter, nor does the averaging of the two frequencies<sup>34,35</sup> improve the correlation in our case.

Finally, we investigated the relationship between the symmetrical and antisymmetrical frequencies since several similar correlations have been reported<sup>2,38</sup>, a restricted one even in the case of aliphatic nitro compounds<sup>15</sup>. However, no correlation was found with *meta* and *para* substituted nitrobenzenes in the solid state spectra<sup>20</sup>, nor with substituted benzoate anions<sup>35</sup>. Fig. 4 reveals again a poor correlation with some big deviations although for *para* derivatives a broken correlation line, as reported by Kross and Fassel<sup>7</sup>, can be confirmed. Relationships between the symme-



trical and antisymmetrical frequencies evidently yield an overall linear graph, but do not apply to relatively small shifts due to remote substituents.

The  $a_1$  band at  $858\text{ cm}^{-1}$  is now usually assigned to the  $\text{NO}_2$  symmetrical deformation mode<sup>11,14</sup>, with a possible contribution from the  $a_1$  ring vibration<sup>12</sup> or C—N stretching<sup>10</sup> mode, although the original assignment<sup>6</sup> to C—N stretching is still advocated<sup>13</sup>. A relatively small sensitivity to substitution has been reported<sup>15,18</sup> and substantiated on a theoretical model<sup>13</sup>. Our data showed that this frequency is changed with substitution over a range of c.  $50\text{ cm}^{-1}$  with some exceeding values, which, of course, may be caused partly by wrong assignment (Fig. 5). The frequencies of *para* derivatives are much less variable and their dependence on  $\sigma$  constants gives a picture similar to Fig. 2, while the points for *meta* derivatives are more scattered and include higher as well as lower values. Notwithstanding the whole pattern of Fig. 5 is compatible with the assumption that the frequency belongs to the  $\text{NO}_2$  group.

The  $b_1$  band at  $704\text{ cm}^{-1}$  has been assigned to  $\text{NO}_2$  out-of-plane deformation<sup>9</sup> or wagging mixed with the  $\gamma(\text{CH})$  "umbrella" deformation mode<sup>14</sup>. An alternative explanation is that it belongs to the  $b_1$  out-of-plane ring deformation and is not connected with the  $\text{NO}_2$  group<sup>10,11</sup>. The dependence on substitution has been followed in a limited range only<sup>9</sup>. Our data (in Nujol) revealed a unique type of relationship shown in Fig. 6. A given substituent has a similar but somewhat larger effect from the *para* as from the *meta* position, shifting the frequency always to higher values. There are again some unexplained deviations, which may be even be due to a wrong

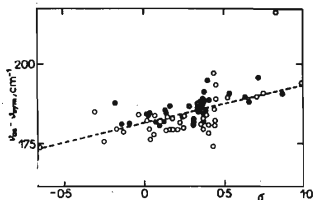


FIG. 3

Hammett Plot of the Difference  $\nu_{as} - \nu_s$  of the  $\text{NO}_2$  Group

Derivatives:  $\circ$  *para*,  $\bullet$  *meta*, the line estimated.

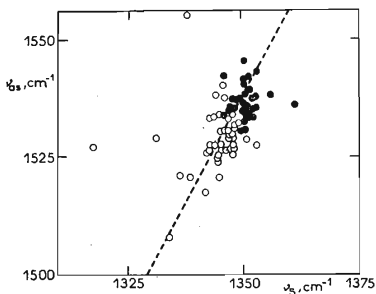


FIG. 4

Plot of the  $\text{NO}_2$  Antisymmetrical vs Symmetrical Stretching Frequency

Derivatives  $\circ$  *para*,  $\bullet$  *meta* the line estimated).

assignment. However, a non-linear relationship is perceptible. The same behaviour is observed with substituents of all types and no simple relationship of their nature to the intensity of the effect is evident. In particular there is no relation to their mass or electronic effects, substituents with or without a free  $\alpha$ -electron pair behave in the same way. This picture is in our opinion not compatible with the assignment of this band to any vibration of the  $\text{NO}_2$  group. In this case the shifts should either be correlated with  $\sigma$  constants (i.e. clearly different for a donor group in the *meta* and *para* position), or the *meta* effect should appear. Hence we believe that our findings confirm the assignment of this band to a ring deformation<sup>10,11</sup>; the frequency shifts express essentially the direct action of the substituent on the benzene ring, the relative position of the  $\text{NO}_2$  group being of secondary importance.

There is a similar disagreement in the literature<sup>8,10-12,14</sup> concerning the band at  $681\text{ cm}^{-1}$ . In this case the reported rough correlation with  $\sigma$  constants<sup>8</sup> suggests a significant contribution from the  $\text{NO}_2$  symmetrical deformation mode<sup>10,12,14</sup>, however, it does not agree with the small isotope effect<sup>11</sup>.

Intensities of the infrared bands were suggested as a measure of substituent effects, particularly the mesomeric ones<sup>2</sup>, and many correlations with reactivity parameters have been described<sup>3</sup>. Their advantage is that no *meta* effect is exhibited<sup>3,2</sup>, a disadvantage is always the low experimental accuracy, when compared to the frequencies. Boček and Zahradník attempted to overcome this difficulty by replacing the absolute values by the ratio of extinction coefficients of the  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  bands<sup>2,6</sup>.

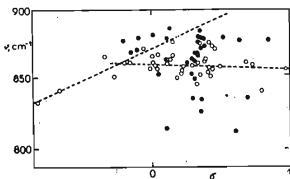


FIG. 5

Hammett Plot of the  $\text{NO}_2$  Symmetrical Deformation Frequency (at  $858\text{ cm}^{-1}$ )

Derivatives:  $\circ$  *para*,  $\bullet$  *meta*.

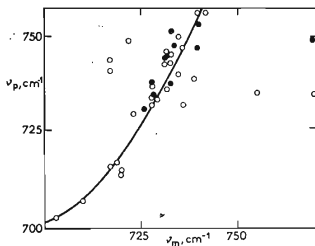


FIG. 6

Plot of the Frequency at  $704\text{ cm}^{-1}$ , *para* vs *meta* Derivatives

$\bullet$  Substituents with a lone electron pair in the  $\alpha$ -position,  $\circ$  other substituents, the curve estimated.

Our experimental intensities of the  $\text{NO}_2$  antisymmetrical and symmetrical vibrations (Table I) agree only fairly with those of Conduit<sup>17</sup> for eight derivatives. For correlations with  $\sigma$  constants a plot of the square roots<sup>39</sup>  $\sqrt{A}$  is certainly better founded than<sup>3</sup> of  $\log A$ , however, the difference is not significant in practice. The plot of  $\sqrt{A_{as}}$  vs  $\sigma$  (Fig. 7) reveals no apparent regularity, although a kind of *meta*-effects seems to exist. A plot of  $\sqrt{A_s}$  (Fig. 8) gives essentially the same picture although it resembles somewhat Fig. 2. The plot of  $\sqrt{A_{as}}/\sqrt{A_s}$  corresponding to the  $q$  index of Boček and Zahradník<sup>26</sup> is not much different. In all the intensity correlations the most striking feature are large differences between quite similar substituents, e.g.  $\text{OSO}_2\text{CH}_3$  and  $\text{OSO}_2\text{C}_6\text{H}_5$ ,  $\text{CON}(\text{CH}_3)_2$  and  $\text{CON}(\text{C}_2\text{H}_5)_2$  etc. The reasons may be similar as in the case of the frequencies, combined with the experimental uncertainty and neighbourhood of other bands. Conduit expected a lowering of the intensities of both  $\nu_{as}$  and  $\nu_s$  bands by electron-attracting substituents but was unable to find experimental proof in his limited set of data<sup>17</sup>, while Brown predicted that the  $\nu_s$  band would be more effected, chiefly by donor groups<sup>15</sup>. Our experiments agree with the latter prediction, as shown in Fig. 8. Substituents capable of conjugation show enhanced values, which might be correlated with some constants of the  $\sigma_R^+$  type if appropriate values were available. There are, however, deviations even from this regularity. On the other hand intensities of the  $\nu_s$  band in the Raman spectrum depend more on substitution even if in a not quite regular manner<sup>24,25</sup>. It seems that in relatively rare cases all the conditions are met to give a meaningful correlation between infrared intensities and substituent polar effects<sup>32,39</sup>.

Summarizing our results we can draw the conclusion that even the characteristic frequencies (*i.e.* relatively mass insensitive) are influenced by several other factors

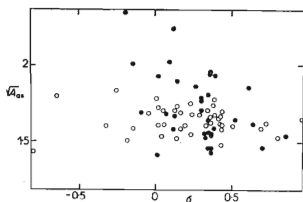


FIG. 7

Hammett Plot of the Intensity of the  $\text{NO}_2$  Antisymmetrical Stretching Frequency

Derivatives:  $\circ$  *para*,  $\bullet$  *meta*.

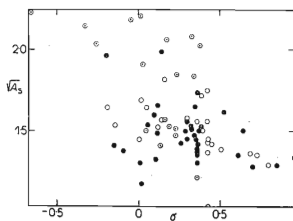


FIG. 8

Hammett Plot of the Intensity of the  $\text{NO}_2$  Symmetrical Stretching Frequency

Derivatives:  $\circ$  *para*,  $\odot$  *para* with lone electron pair or  $\alpha$ -C=C double bond,  $\bullet$  *meta*.

in addition to substituent polar effect. In particular the *meta* effect is striking, although its nature is still unknown; individual large deviations are also rather common. Hence correlations of infrared frequencies with reactivity parameters<sup>3,4</sup> must be viewed cautiously, in particular they cannot be recommended for determining new values of constants. On the other hand a careful analysis of these correlations based on broad experimental material may be useful when frequencies are assigned and their dependence on substitution studied.

## REFERENCES

1. Exner O., Svátek E.: This Journal 36, 534 (1971).
2. Bellamy L. J.: J. Chem. Soc. 1955, 4221.
3. Rao C. N. R., Venkataraghavan R.: Can. J. Chem. 39, 1757 (1961).
4. Leffler J. E., Grundwald E.: *Rates and Equilibria of Organic Reactions*, p. 255. Wiley, New York 1963.
5. Exner O.: This Journal 31, 65 (1966).
6. Randle R. R., Whiffen D. H.: J. Chem. Soc. 1952, 4153.
7. Kross R., Fassel V. A.: J. Am. Chem. Soc. 78, 4225 (1956).
8. Uhlich U., Kresze G.: Z. Anal. Chem. 182, 81 (1961).
9. Garrigou-Lagrange C., Chehata M., Sourisseau G.: J. Chim. Phys. 62, 261 (1965).
10. Green J. H. S., Kynaston W., Lindsey A. S.: Spectrochim. Acta 17, 486 (1961).
11. Pinchas S., Samuel D., Silver B. L.: Spectrochim. Acta 20, 179 (1964).
12. Farmer V. C.: Spectrochim. Acta 23 A, 728 (1967).
13. Novikov S. S., Šljapočnikov V. A., Oleneva G. I., Konšev V. A., Osipov V. G.: Ž. Fiz. Chim. 44, 2718 (1970).
14. Green J. H. S., Harrison D. J.: Spectrochim. Acta 26 A, 1925 (1970).
15. Brown J. F.: J. Am. Chem. Soc. 77, 6341 (1955).
16. Van Veen A., Verkade P. E., Wepster B. M.: Rec. Trav. Chim. 76, 801 (1957).
17. Conduit C. P.: J. Chem. Soc. 1959, 3273.
18. Katritzky A. R., Simmons P.: Rec. Trav. Chim. 79, 361 (1960).
19. Gherseti S.: Boll. Sci. Fac. Chim. Ind. Bologna 21, 228 (1963).
20. Hamer J., Placek L., Ahmad M.: *Nitro Compounds*, p. 395. Proc. Inter. Symp., Warsaw 1963; Chem. Abstr. 64, 162 (1966).
21. Yates K., Thompson A. A.: Can. J. Chem. 45, 2997 (1967).
22. Kristián P., Kováč Š., Hritzová O.: This Journal 34, 563 (1969).
23. Lindberg B. J., Schröder B.: Acta Chem. Scand. 24, 3089 (1970).
24. Šorygin P. P., Roščupkin V. P., Petuchov V. A., Egorova Z. S.: Ž. Fiz. Chim. 35, 258 (1961).
25. Bobovič J. S., Beljaevskaja N. M.: Optika i Spektroskopija 19, 198 (1965).
26. Boček K., Zahradník R.: Spectrochim. Acta 18, 564 (1962).
27. Exner O., Jehlička V., Uchytíl B.: This Journal 33, 2862 (1968).
28. Smith G. G., Jones D. A. K.: J. Org. Chem. 28, 3496 (1963).
29. Looker J. H.: J. Org. Chem. 17, 510 (1952).
30. Halmann H., Pinchas S.: J. Chem. Soc. 1960, 1246.
31. Exner O. in the book: *Advances in Linear Free Energy Relationships* (N. B. Chapman, J. Shorter, Eds). Plenum Press, London 1972.
32. Exner O., Boček K.: Tetrahedron Letters 1967, 1433.
33. Herzberg G.: *Molecular Spectra and Molecular Structure*, p. 115. van Nostrand, Princeton 1956.

34. Lindberg B. J.: Acta Chem. Scand. 22, 571 (1968).
35. Dunn G. E., McDonald R. S.: Can. J. Chem. 47, 4577 (1969).
36. Lindberg B. J.: Acta Chem. Scand. 21, 2215 (1967).
37. Katritzky A. R.: *Physical Methods in Heterocyclic Chemistry*, Vol. II, p. 308. Academic Press, New York 1963.
38. Bellamy L. J., Williams R. L.: J. Chem. Soc. 1957, 863.
39. Brown T. L.: J. Phys. Chem. 64, 1798 (1960).

Translated by the author (O. E.).