influence. It is possible, however, that a more refined analysis of the ortho effect, such as that suggested by Charton,[40] would lead to a somewhat diminished contribution from the steric component.

Registry No. **3a**, 67962-17-8; **3b**, 67962-16-7; **3c**, 67962-18-9; **3d**, 29569-91-3; **3e**, 67962-23-6; **3f**, 67962-20-3; **3g**, 103457-25-6; **4a**, 22965-99-7; **4b**, 22966-01-4; **4c**, 22966-06-9; **4d**, 614-47-1; **4e**, 22966-11-6; **4f**, 22966-10-5; **4g**, 53744-31-3; **5a**, 2834-10-8; **5b**, 2698-44-4; **5c**, 2698-43-3; **5d**, 2700-22-3; **5e**, 2698-41-1; **5f**, 2698-42-2; **5g**, 2826-30-4; **6a**, 6768-22-5; **6b**, 24331-75-7; **6c**, 2262-52-4; **6d**, 5292-53-5; **6e**, 6768-20-3; **6f**, 93098-67-0; **6g**, 17422-56-9; **7a**, 14533-89-2; **7b**, 24393-41-7; **7c**, 103457-26-7; **7d**, 2169-69-9; **7e**, 24393-43-9; **7f**, 103457-27-8; **7g**, 68792-18-7; **8a**, 103457-28-9; **8b**, 103457-29-0; **8c**, 103457-30-3; **8d**, 101220-25-1; **8e**, 103457-31-4; **8f**, 103457-32-5; **8g**, 103457-33-6; **9a**, 24393-54-2; **9b**, 24393-48-4; **9c**, 89760-42-9; **9d**, 4192-77-2; **9e**, 24393-51-9; **9f**, 91047-77-7; **9g**, 24393-59-7; **10a**, 103457-34-7; **10b**, 103457-35-8; **10c**, 103457-36-9; **10d**, 17434-21-8; **10e**, 103457-37-0; **10f**, 103457-38-1; **10g**, 51813-41-3; **11a**, 57103-26-1; **11b**, 26155-19-1; **11c**, 91319-60-7; **11d**, 1885-38-7; **11e**, 51220-00-9; **11f**, 51220-04-3; **11g**, 51991-49-2; **12a**, 57103-24-9; **12b**, 57103-23-8; **12c**, 91319-61-8; **12d**, 24840-05-9; **12e**, 51219-99-9; **12f**, 51220-03-2; **12g**, 74845-04-8.

Supplementary Material Available: Tables showing multiple correlation coefficients for analyses of β-carbon chemical shifts with two- and three-parameter equations, *F* values for two- and three-parameter correlations, and the estimated error in the steric parameter for three-parameter correlations (5 pages). Ordering information is given on any current masthead page.

Notes

Resonance and Solvent Effects on Absorption Spectra. 4. Effects of 5-Substituents on Electronic Spectra of Some 2-Nitroaniline Derivatives

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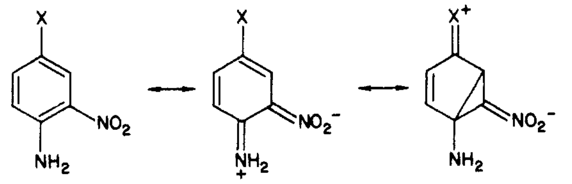
Received June 4, 1985

In Part 3 of this series,[1] we reported that positions of [$>N^+{=}C(1) \rightarrow C(2){=}NO_2^-$] bands in the electronic spectra of some 4-X-2-nitroaniline derivatives (**1**) were well correlated (r = 0.994–0.998) by dual substituent parameter (dsp) equations involving σ_I and σ_R^+. The multiple linear regression equations in cyclohexane (CH) and dimethylformamide (DMF) were given by eq 1a,b.

$$\nu(1)_{\max}{}^{CH} = 26.42 + 1.84\sigma_I + 2.44\sigma_{R^+} \times 10^3 \text{ cm}^{-1} \quad (1a)$$

$$\nu(1)_{\max}{}^{DMF} = 24.39 + 2.05\sigma_I + 2.38\sigma_{R^+} \times 10^3 \text{ cm}^{-1} \quad (1b)$$

That σ_{R^+} in eq 1a,b resulted in better statistical goodness of fit than σ_{R° or σ_{R^-} was rationalized on the basis that, in addition to primary canonical structures like **1a**, there are



1 1a 1b

also important resonance contributions to the electronic excited states by meta-bridged canonical structures like **1b**, wherein positive charge is delocalized from the amine nitrogen to π-donor substituents in the 4-position.

Similar *meta*-quinoidal structures had earlier been invoked by Kamlet et al.[2] to rationalize solvent and substituent effects on 3-nitroaniline spectra, by Porto et al. to rationalize substituent effects on 2-nitrodiphenyl sulfide spectra,[3] and by Rapoport et al.[4] in connection with nitrophenol spectra.

The excellent fit to eq 1a,b accorded with an earlier suggestion by Brownlee and Topsom[5] that UV/visible spectra should follow high-precision linear free energy relationships only when the substituents being varied are external to the chromophore being measured.

The present investigation is an extension of the earlier work to the 5-X-2-nitroanilines (**2**), where the substituent being varied is again external to the chromophore being studied. This time, however, the substituents are meta to the amino and para to the nitro group.

Experimental Section

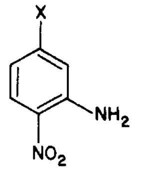
Materials. Samples were prepared by the methods described in the literatures. All solvents were purified by removing acidic or basic impurities, through drying and taking a narrow cut of fractional distillate.

UV–Visible Spectra. The instrument was Hitachi 220A double-beam spectrometer. Measurements were carried out four times at each of three different concentrations at 25 °C.

^{15}N NMR Spectra. Measurements were made with JEOL FX90Q FT-NMR spectrometer at ^{15}N natural-abundance level using $HCONH_2$ as external standard at room temperature. Samples were run as 1.7 M Me_2SO-d_6 solution.

Results and Discussion

Positions of $\nu_{\max}$ for the lowest energy transitions in the spectra of eight 5-X-2-nitroanilines (**2**) are assembled in



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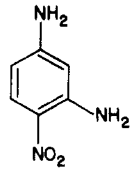

2'

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[1] Yokoyama, T.; Taft, R. W.; Kamlet, M. J. *Spectrochim. Acta* **1984**, *40A*, 669.

(2) Kamlet, M. J.; Jones, M. E.; Taft, R. W.; Abboud, J.-L. M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 342.

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0022-3263/86/1951-3540$01.50/0

Table I. Ultraviolet/Visible Spectral Data ($\nu_{max} \times 10^3$ cm^{-1})[a] for 5-X-2-NO_2PhNH_2 (2) and 5-X-2-NO_2PhSPh (4)

subst	$\nu(2)_{max}{}^{CH}$	$\nu(2)_{max}{}^{DMF}$	$\nu(4)_{max}{}^{MeOH\,c}$	$\sigma_I{}^d$	$\sigma_R{}^d$	$\sigma_{R^\circ}{}^d$
NH_2	27.35	(25.80)[e]		0.12	−0.48	−0.48
OMe	27.36	25.39	28.25	0.27	−0.45	−0.45
Me	26.59	24.47	27.40	−0.04	−0.11	−0.11
Cl			27.78	0.46	−0.23	−0.23
Br			27.70	0.44	−0.19	−0.19
I			27.47	0.39	−0.11	−0.16
H	26.48	24.35	27.32	0.00	0.00	0.00
COOMe	25.45	23.48	26.32	0.30	0.34	0.14
COOEt	25.44	23.54		0.30	0.34	0.14
$COCH_3$	25.15	23.28		0.28	0.47	0.16
CN			26.46	0.56	0.33	0.13
CF_3	26.53[b]		27.32[b]	0.45	0.17	0.08
NO_2	24.98	22.81		0.65	0.46	0.15

[a] CH = cyclohexane, DMF = dimethylformamide. [b] Not included in correlation. [c] Reference 3, calculated as ν_{max} values. [d] Reference 6. [e] Unsymmetrical band, indicating overlap with high-intensity lower wavelength band; see text.

Table I together with the substituent σ_I σ_{R°, and σ_{R^-} values.[6] The spectrum of 5-amino-2-nitroaniline (2′) in DMF (but not in CH) differs from the other spectra and is excluded from the correlations that follow because of an unsymmetrical band shape and a high absorption intensity for the lowest energy band (ϵ 19,000, compared with 5000–6000 for the other compounds studied) which suggests that there is overlap between the [$>N^+{=}C(1) \rightarrow C(2){=}NO_2^-$] band being studied and a higher intensity, higher energy [$>N^+{=}C(1) \rightarrow C(4){=}NO_2^-$] band. [Spectra of **2** above 300 nm consist of two bands attributable to p → π^* transitions: a longer wavelength, lower intensity band arising from a C(1) → C(2) ortho transition and a shorter wavelength higher intensity band arising from a C(1) → C(4) para transition.]

It is seen in Table I that the 5-NO_2 substituent causes a bathochromic (lower energy) shift, relative to X = H, of 1.50×10^3 cm^{-1} in CH, whereas the 5-NH_2 substitent causes a hypsochromic (higher energy) shift of 0.87×10^3 cm^{-1}. This is in marked contradistinction to the case for the 4-X-2-nitroanilines,[1] where the π-donor substituents had caused the bathochromic shifts and the π-acceptor substituents had led to generally smaller hypsochromic shifts, and suggests that the highest quality correlations should be the σ_{R^-} or with σ_I and σ_{R^-}.

Accordingly, the linear regressions of $\nu(2)_{max}$ with σ_{R^-} are given by eq 2a,b, and the dsp correlations with σ_{R^-} and σ_I

$$\nu(2)_{max}{}^{CH} = (26.28 \pm 0.04) - (2.46 \pm 0.11)\sigma_{R^-} \times 10^3\ \mathrm{cm}^{-1} \quad (2a)$$

$$n = 8,\ r = 0.9936,\ \mathrm{sd} = 0.118^{7}$$

$$\nu(2)_{max}{}^{DMF} = (24.25 \pm 0.21) - (2.41 \pm 0.21)\sigma_{R^-} \times 10^{-3}\ \mathrm{cm}^{-1} \quad (2b)$$

$$n = 7,\ r = 0.9810,\ \mathrm{sd} = 0.180$$

are given by eq 3a,b. Despite the seemingly better cor-

$$\nu(2)_{max}{}^{CH} = (26.38 \pm 0.04) - (0.50 \pm 0.15)\sigma_I - (2.31 \pm 0.08)\sigma_{R^-} \times 10^3\ \mathrm{cm}^{-1} \quad (3a)$$

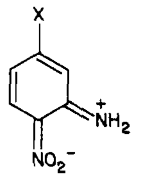
$$n = 8,\ r = 0.9980,\ \mathrm{sd} = 0.072^{7}$$

$$\nu(2)_{max}{}^{DMF} = (24.37 \pm 0.08) - (0.59 \pm 0.31)\sigma_I - (2.24 \pm 0.20)\sigma_{R^-} \times 10^3\ \mathrm{cm}^{-1} \quad (3b)$$

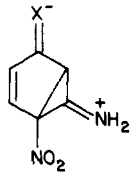
$$n = 7,\ r = 0.9900,\ \mathrm{sd} = 0.147$$

relations by eq 3a,b, the terms in σ_I are statistically significant at only the 92 and 87% confidence levels (by the Student's t-test). It is generally considered that to warrent inclusion of an additional term in a multiple linear regression equation, the confidence level needs to be 95% or greater, and on this basis eq 2a,b are the preferred correlation equations for $\nu(2)_{max}$. For comparison with eq 2a,b, the measures of goodness of fit for correlations with other sets of substituent parameters are as follows: σ_{R°(CH), $r = 0.946$, sd = 0.34; σ_{R°(DMF), $r = 0.927$, sd = 0.35; σ^-(CH), $r = 0.967$; σ^-(DMF), $r = 0.957$; σ°(CH), $r = 0.962$; σ°(DMF), $r = 0.950$. The high precision of the correlations again confirms Brownlee and Topsom's observation[5] that high-quality Hammett-type correlations of UV/visible spectral shifts are likely only when the substituents being varied are external to the chromophore being studied.

It is of interest that the coefficients of the independent variables have positive signs in eq 1a,b and negative signs in eq 3a,b, which means that the same substituents have exactly opposite effects on [$>N^+{=}C(1) \rightarrow C(2){=}NO_2^-$] electronic transitions depending on whether they are in the 4- or 5-position. Further, the better quality correlations with σ_{R^-} than with σ_{R° suggest that again "*meta*-quinoidal" canonical structures like **2b** are important resonance contributors to the electronic excited states. Interestingly, the effect of the quinoidal structure is to disperse positive charge in **1b** and negative charge in **2b**.



2a



2b

It is of interest to compare the coefficients of the independent variables in eq 1a,b and 2a,b. The similar magnitudes of the terms in σ_{R^+} in the former equations and the terms in σ_{R^-} in the latter suggest that comparable effects on ν_{max} arise from mesomeric delocalization of the positive charge from amine nitrogen to π-donor substituent in the 4-position, as in structures **1a** ↔ **1b**, and of the negative charge from nitro oxygens to π-acceptor substituents in the 5-position, as in **2a** ↔ **2b**. This suggests, in turn, that meta-bridged structures are comparable resonance contributors to the lowest excited states of **1** and **2**.

The situation regarding the inductive terms is more complex. Although not statistically significant in eq 3a,b, the terms in σ_I are significant at the 98.5 and 99% confidence levels in eq 1a,b. The positive coefficients of σ_I in eq 1a,b indicate that the effects of inductive electron withdrawal by 4-substituents in series 1 are hypsochromic, whereas the corresponding inductive effects of 5-substituents, if any, are very much smaller and bathochromic.

Spectra of 5-X-2-Nitrodiphenyl Sulfides. Additional useful information may be gained by comparing eq 2a,b and an equation we had reported earlier for 4-substituted 2-nitrodiphenyl sulfides (**3**) with the equations describing substituent effects in 5-substituted 2-nitrodiphenyl sulfides

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[6] Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 13.

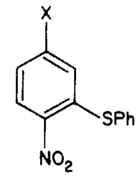
[7] The result for X = CF_3 in cyclohexane was out of line and was excluded from the correlations. If included, $r = 0.963$, sd = 0.26 for eq 2a, and $r = 0.963$, sd = 0.28 for eq 3a.

[8] If the result for X = CF_3 is included, $r = 0.958$, sd = 0.17 for eq 5a, and $r = 0.947$, sd = 0.20 for eq 5b.

(4). The earlier correlation for series **3** was given by eq 4.

$$\nu(\mathbf{3})_{\max}{}^{\mathrm{MeOH}} = 27.28 + 0.61\sigma_{\mathrm{I}} + 2.36\sigma_{\mathrm{R^+}} \times 10^3\ \mathrm{cm^{-1}} \quad (4)$$

Values of $\nu_{\max}$ for the lowest energy bands of **4** are also assembled in Table I. The data are those of Porto and co-workers[3] and are for spectra in methanol. As with series **2**, the result for X = CF_3 is out of line and is excluded from the correlations. The regression equation with $\sigma_{\mathrm{R^-}}$ and the dsp equation with σ_{I} and $\sigma_{\mathrm{R^-}}$ are given by eq 5a,b. It is seen that, as before, the term in σ_{I} is statistically insignificant, and we conclude that inductive electronic effects in series **4** are even less important than in series **2**. Indeed, the correlation equations for the 4- and 5-substituted 2-nitrodiphenyl sulfides, eq 4 and 5a, bear similar relationships to one another as was observed with the 4- and 5-substituted 2-nitroanilines, i.e., similar coefficients of $\sigma_{\mathrm{R^+}}$ in eq 4 and $\sigma_{\mathrm{R^-}}$ in eq 5 and a greater dependence on inductive effects of 4-substituents than 5-substituents.



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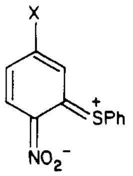
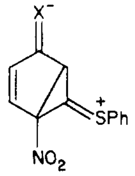


4a



4b

$$\nu(\mathbf{4})_{\max}{}^{\mathrm{MeOH}} = (27.21 \pm 0.04) - (2.39 \pm 0.09)\sigma_{\mathrm{R^-}} \times 10^3\ \mathrm{cm^{-1}} \quad (5a)$$

$$n = 8,\ r = 0.9953,\ \mathrm{sd} = 0.068^{8}$$

$$\nu(\mathbf{4})_{\max}{}^{\mathrm{MeOH}} = (27.20 \pm 0.05) - (0.03 \pm 0.13)\sigma_{\mathrm{I}} - (2.39 \pm 0.10)\sigma_{\mathrm{R^-}} \times 10^3\ \mathrm{cm^{-1}} \quad (5b)$$

$$n = 8,\ r = 0.9954,\ \mathrm{sd} = 0.074^{8}$$

We again rationalize the substituent effects, as did Porto et al.,[3] by contributions to the electronic excited states by *meta*-quinoidal structures like **4b**, wherein negative charge is delocalized from the nitro oxygens to π-acceptor substituents in the 5-position. It is noteworthy that, although the total electronic excited states have significantly different energies, as evidenced by the different $\nu_{\max}$ values for the parent compounds, the similar coefficients of $\sigma_{\mathrm{R^-}}$ in eq 2a,b and 5a suggest that the contributions of the meta-bridged structures **2b** and **4b** to those excited states are similar (which is to us an unexpected result).

^{15}N NMR Spectra of 5-X-2-Nitroaniline Derivatives. We have also determined the one-bond ^{15}N–H coupling constants and amine nitrogen chemical shifts $\delta(^{15}N)$ of some derivatives of **2** in Me_2SO-d_6. Results are as follows (δ values upfield from $HCONH_2$ external standard):

5-subst	$^1J(^{15}NH)$, Hz	$\delta(^{15}N)$
MeO	92.2	−32.0
Me	92.8	−34.6
H	92.2	−34.6
$COCH_3$	91.4	−33.0
CF_3	92.1	−31.5
NO_2	91.3	−29.8

The very similar coupling constants indicate that hybridization is very near sp^2, irrespective of whether the 5-substituent is a π acceptor or a π donor (just as was the case with the 4-X-2-nitroanilines).[1,9] The best correlation of the $\delta(^{15}N)$ values is given by eq 6.

$$\delta(^{15}\mathrm{N}(\mathbf{2})) = (-34.63 \pm 0.14) + (7.46 \pm 0.38)\sigma_{\mathrm{I}} - (1.51 \pm 0.43)\sigma_{\mathrm{R^\circ}} \quad (6)$$

$$n = 6,\ r = 0.9962,\ \mathrm{sd} = 0.210$$

It is evident that the NMR results follow a predominantly inductive progression with only a minor mesomeric contribution, which is not unexpected, as here we are dealing with ground-state phenomenology, whereas with the UV/visible spectra we were dealing with predominantly electronic excited-state phenomenology. As before,[1] we encounter here a situation where a ground-state property of a given indicator is best correlated by one set of substituent parameters, while an excited-state property is best correlated by another set. We will discuss these results further in a future paper dealing with ^{15}N NMR spectra of 4-substituted 2-nitroaniline derivatives.

Acknowledgment. The work by M.J.K. was done under the Naval Surface Weapons Center Foundational Research Program. We acknowledge the assistance of Kazuhiro Matsushita (JOEL Ltd.) and Yoshiharu Yoneyama who measured the ^{15}N NMR spectra and Issei Kasahara who prepared the samples.

Registry No. **2** (X = MeO), 16133-49-6; **2** (X = Me), 578-46-1; **2** (X = H), 88-74-4; **2** (X = Ac), 79127-41-6; **2** (X = CF_3), 402-14-2; **2** (X = NO_2), 619-18-1; **2** (X = NH_2), 5131-58-8; **2** (X = Cl), 1635-61-6; **2** (X = Br), 5228-61-5; **2** (X = I), 20289-35-4; **2** (X = C(O)OMe), 99512-09-1; **2** (X = C(O)OEt), 84228-43-3; **2** (X = CN), 99512-10-4; **4** (X = MeO), 1696-40-8; **4** (X = Me), 33358-44-0; **4** (X = Cl), 33358-41-7; **4** (X = Br), 33358-42-8; **4** (X = I), 33358-43-9; **4** (X = H), 4171-83-9; **4** (X = C(O)OMe), 33358-40-6; **4** (X = CN), 33358-39-3; **4** (X = CF_3), 33358-45-1; ^{15}N, 14390-96-6.

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Quantitation of *N*-(2-Hydroxy-4-methoxyphenyl)glyoxylohydroxamic Acid, a Reactive Intermediate in Reactions of 2,4-Dihydroxy-7-methoxy-1,4-benzoxazin-3-one

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Extracts of various Gramineae contain hydroxamic acids such 2,4-dihydroxy-7-methoxy-1,4-benzoxazin-3-one (DIMBOA), which are involved in the resistance of the plants to pests and pathogens.[1,2] It was suggested that the toxicity of DIMBOA is partly due to reactions of its open-chain isomer, *N*-(2-hydroxy-4-methoxyphenyl)glyoxylohydroxamic acid (**1**).[3,4] On the basis of rate and product studies,[5-7] this intermediate has been invoked in the decomposition reaction of DIMBOA. Since **1** has electroactive groups different from those of DIMBOA, we attempted its quantitation by polarographic reduction of

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