Resonance Raman Studies of *para*-Substituted *NN*-Dimethylaniline Free Radical Cations

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A series of *para*-substituted *NN*-dimethylaniline free radical cations have been formed as reaction intermediates in the chemical oxidation of their neutral parent compounds. The free radical cations all possess intense visible absorptions which have facilitated the excitation of their resonance Raman spectra. The parent-to-radical Raman wavenumber shifts have been interpreted in terms of the structure and bonding changes that occur upon radical formation. The changes observed do not correlate well with the Hammett (σ_p) values for the *para*-substituents.

A NATURAL extension of our previous study of a series of *para*-substituted aniline free radical cations [1] was to investigate the effects brought about by methylation of the nitrogen atom. Accordingly, a series of *para*-substituted *NN*-dimethylaniline free radical cations was prepared. As before, very little was known about the vibrational spectra of the neutral parent compounds and no structural information or vibrational assignments were known for the parents. However, the stable *NNN'N'*-tetramethyl-*p*-phenylenediamine (TMPD) radical cation (Wurster's blue) has been extensively studied,[2-4] as has the *NN*-dimethyl-*p*-phenylenediamine (DMPD) radical cation (Wurster's red).[5,6] The crystal structures of both these species are well established, although few data are available concerning their neutral parents.

We present here the resonance Raman spectra of three *para*-substituted *NN*-dimethylaniline free radical cations $\{[(CH_3)_2NC_6H_4X]^{+\cdot}$, X = NH_2, OCH_3, and $OC_2H_5\}$ and the Raman spectra of their parents. These data have been compared with the previous Raman data from both the TMPD system [3,4] and the donor–acceptor *para*-substituted *NN*-dimethylaniline radical cations {*e.g.* $[(CH_3)_2NC_6H_4CN]^{+\cdot}$}.[7] Tentative assignments of the spectra of the radical cations are offered. An attempt to correlate the wavenumber shifts observed for the ring C–N stretching mode with the Hammett σ_p values of the *para*-substituents is made. The magnitudes of these positive wavenumber shifts are compared with those observed for the previously reported series of *para*-substituted anilines.[1] All the free radicals studied exhibit broad optical absorption bands in a region of the visible spectrum that is well served by our step-tunable lasers. This allowed us to excite the free radical resonance Raman spectra at several different wavelengths and to plot their excitation profiles.

EXPERIMENTAL

p-Methoxy- and *p*-ethoxy-*NN*-dimethylaniline were prepared by methylation of their respective parent anilines.[8] The products were recrystallized from ethanol and purified by vacuum sublimation. Their purity was checked using m.p.s and n.m.r. spectra. They were then stored in a refrigerator under nitrogen atmosphere. *NN*-Dimethyl-*p*-phenylenediamine (Hopkin and Williams; fine chemicals grade) was purified by vacuum sublimation and stored under nitrogen in a refrigerator before use. Ethanol (Burrough; analytical reagent) and ethanediol (Merck; *pro analysi*) were used as supplied; water was doubly distilled.

The free radical cations were formed in two ways, (i) by photoionization of the parent compounds contained in ethanol glasses at 77 K and (ii) by chemical oxidation, at room temperature, of solutions of the parent compounds. The former route to free radical formation and the subsequent bleaching experiments were essentially as for the *para*-substituted anilines.[1] Using a 200 W Wotan H.B.O. super pressure Hg lamp,[1] irradiation times between 5 and 8 min were found to be optimal. The latter method for free radical production involved chemical oxidation of the parents using molecular bromine in ethanol as solvent. The DMPD radical was prepared as previously documented,[6] in alcohol solvent containing acetic acid, and was stable at room temperature when kept under nitrogen. The *p*-methoxy- and *p*-ethoxy-radical cations were unstable (half-lives, $t_{\frac{1}{2}}$ *ca.* 2.5 min) at room temperature and hence were formed in a steady state using a flow technique. Flow rates of 30 cm^3 min^{-1} were found to be optimal. Conditions were optimized by following the optical absorption spectra at different flow rates.

Raman spectra were obtained using the Jobin Yvon Ramanor HG2 spectrometer and data acquisition equipment as detailed previously.[1] The spectra were excited by either krypton or argon ion laser lines. Raman spectra of the solid parent *p*-methoxy- and *p*-ethoxy-compounds were obtained using a rotating disc technique; solution phase spectra were measured from a spinning glass cell. The DMPD parent was very susceptible to air oxidation. In order to avoid this, the spectrum of the solid compound was obtained by placing it in a specially constructed rotating cell which could be flushed with nitrogen and then sealed. The solution phase spectrum was obtained using the standard spinning glass cell; however, this also was flushed with nitrogen before filling and sealing.

The resonance Raman spectra of the free radical *p*-methoxy- and *p*-ethoxy-species were measured either in a low-temperature Raman cell [1] or in an open-flow cell, depending on the method of production used. The DMPD radical cation was stable under certain conditions. Its spectrum was obtained using the spinning glass cell, which was flushed with nitrogen before filling and sealing. Depolarization ratio measurements were made by analysing the scattered light in front of the spectrometer entrance slit.

Electronic absorption spectra of the free radicals were obtained either by using a low-temperature cell [1] for photochemically generated species at 77 K or with the same flow cell as used for the room temperature Raman measurements.

Optical absorption spectra of the DMPD radical cation were recorded hourly to ascertain its stability at room temperature.

I.r. spectra of the parent compounds were recorded from KBr pellets. E.s.r. spectra of irradiated glasses at 77 K were obtained from a Varian E-104 e.s.r. spectrometer. The e.s.r. spectra of the DMPD species were obtained immediately after formation and also 8 h after formation, in order to check its stability.

RESULTS

The u.v.–visible absorption spectra of the purified parent compounds were blank between 400 and 700 nm. However, their free radical cations all showed intense optical absorptions (see Figure 1), which have allowed the excitation of their resonance Raman spectra. These absorptions agreed well with literature data.[6,9] As can be seen from Figure 1, the DMPD radical exhibited an absorption fine structure at 77 K. Only a slight decrease in absorbance was observed at room temperature over 8 h.

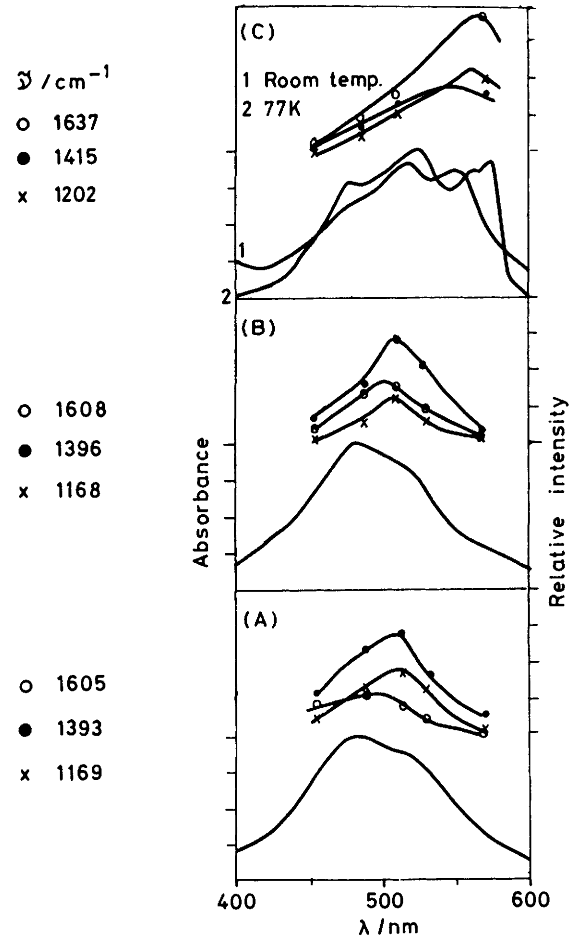

FIGURE 1 Visible absorption spectra for *para*-substituted *NN*-dimethylaniline radical cations, $[(CH_3)_2NC_6H_4X]^{+\cdot}$, together with excitation profiles of some prominent resonance Raman bands. The substituents X are OCH_3 (A), OC_2H_5 (B), and NH_2 (C)

Visible absorption measurements also were made when the u.v. photoionization was performed in an ethanediol–water glass at 77 K. In each case the irradiated glass became a very dark blue colour, with $\lambda_{max.}$ *ca.* 550—600 nm. Subsequent bleaching of the glass, as described previously,[1] left only the absorption spectra of the free radicals.

The e.s.r. measurements on the ethanol matrix containing the trapped free radicals at 77 K all showed only the features previously attributed to the $CH_3\dot{C}HOH$ radical species.[9] The DMPD species, studied at room temperature, exhibited an e.s.r. spectrum which remained unchanged after 8 h under nitrogen. This was used as confirmation of its stability.

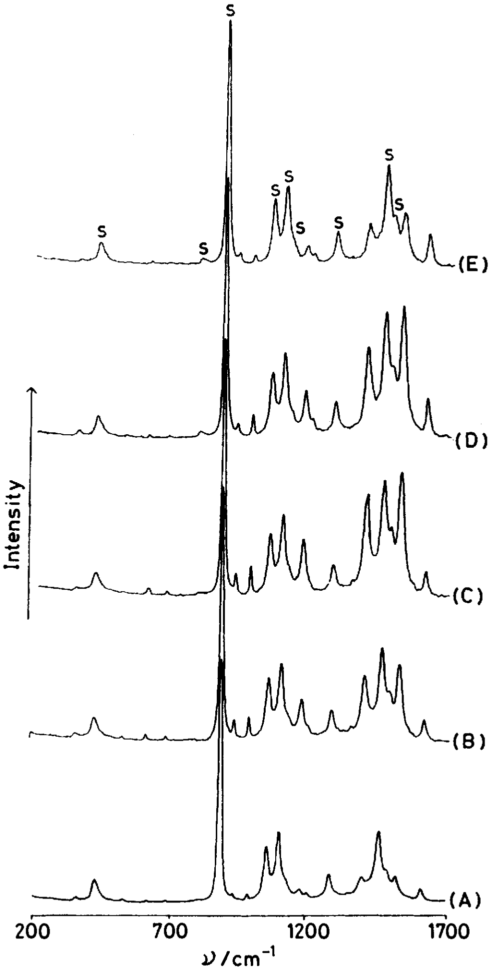

FIGURE 2 Resonance Raman spectra of the *p*-methoxy-*NN*-dimethylaniline radical cation recorded between 200 and 1 700 cm^{-1} using (A) 568.2, (B) 530.9, (C) 514.5, (D) 488.0, and (E) 457.9 nm excitation. All spectra have been digitally smoothed and backgrounds subtracted where necessary. Solvent bands are marked S

Table 1 gives details of the Raman bands recorded between 200 and 1 700 cm^{-1} for each parent and derived free radical species in the solution phase. The resonance Raman spectra of each of the free radical cations were obtained using several different exciting lines, as shown in Figure 2 for the *p*-methoxy-radical cation. The spectra shown in Figure 2 were obtained using a fast flow system. As can be seen, the relative intensities of some bands change quite markedly with different exciting lines. It was found that the *p*-methoxy- and *p*-ethoxy-radicals formed by photoionization

TABLE 1

Raman band wavenumbers (cm^{-1}) of the fundamental modes of DMPD, *p*-methoxy-*NN*-dimethylaniline (PM), and *p*-ethoxy-*NN*-dimethylaniline (PE) parents, and their respective radical cations

DMPD [a]	DMPD$^{+\cdot}$ [b]	DMPD$^{+\cdot}$ −DMPD	PM [a]	PM$^{+\cdot}$ [b]	PM$^{+\cdot}$ −PM	PE [a]	PE$^{+\cdot}$ [b]	PE$^{+\cdot}$ −PE
	1 661 (sh)		1 616s	1 605m-w	−11	1 619s	1 608m	−11
1 624s	1 637s	+13	(1 576) [c]	1 516s	−60	(1 576) [c]	1 516s	−60
1 523w	1 537m	+14	1 336w	1 393s	+57	1 338w	1 369s	+58
1 309w	1 415m-s	+106		1 344w		1 245 (sh)		
1 217w	1 202m-s	−15	1 243 (sh)			1 185s		
1 191m	1 177m	−14	1 183s	1 190 (sh)	+7	1 163m	1 168s	+5
1 150m			1 148 (sh)	1 169s	+21	950m	984m	+36
941w	932w	−9	946m	982m	+46	923w	938m	+15
840 (sh)				930m		811s		
819 (sh)			804s			792 (sh)		
366w	381s	+15	712w			706w		
			681w	688w	+7	638w		
			538w	532w	−6	551w		
			497 (sh)	491w	−6	488w	496w	+12
			350w	365w	+15	397 (sh)		
						301w		
						256 (br)		

s = Strong, m = medium, w = weak, (sh) = shoulder, (br) = broad.

[a] At room temperature in ethanol. [b] At room temperature, formed by bromine oxidation. [c] From spectrum of solid compound.

at 77 K were gradually bleached out when exposed to green laser radiation at powers in excess of *ca.* 50 mW. Because of the low power, the spectra obtained were of poor quality and required multi-scanning to give acceptable signal-to-noise ratios. The DMPD radical cation formed in this way was even more sensitive to the laser beam and bleached at very low laser powers. No resonance Raman spectra were obtained from this radical when formed by photoionization at 77 K. It was, therefore, more convenient for us to use the fast-flow chemical oxidation technique to produce the *p*-methoxy- and *p*-ethoxy-radical cations. The DMPD radical, when prepared as outlined previously, was stable at room temperature and gave no experimental problems. The depolarization ratios were measured for the more intense resonance-enhanced Raman bands in each system studied, and all were found to be *ca.* 1/3.

Assignment of Spectra.—There have been few detailed analyses of the vibrational spectra of molecules containing the $N(CH_3)_2$ group. No vibrational data have been found in the literature concerning the compounds studied here. Therefore assignments have been based on previous studies of similar compounds, namely *p*-*NN*-dimethylaminobenzonitrile,[10] *NN*-dimethylaniline,[10] *NN*-dimethyl-*p*-toluidine,[10] TMPD (parent and radical)[4] and other donor–acceptor *para*-substituted *NN*-methylaniline radical cations and parents.[7] In the absence of any isotopically substituted radical cation data only those assignments involving a high degree of certainty are given (Table 2).

TABLE 2

Assignment of resonance Raman bands for the DMPD, *p*-methoxy-*NN*-dimethylaniline (PM), and *p*-ethoxy-*NN*-dimethylaniline (PE) radical cations formed by chemical oxidation at room temperature

Wavenumber (cm^{-1})					
DMPD$^{+\cdot}$	PM$^{+\cdot}$	PM$^{+\cdot}$ [a]	PE$^{+\cdot}$	PE$^{+\cdot}$ [a]	Assignment [b]
1 661					
1 637	1 605		1 608		Ring C–C (8a)
1 537	1 516	1 518	1 516	1 518	Ring C–C (8b) or (19a)
1 415	1 393	1 390	1 396	1 388	ν(CN) (7a)
	1 344				
1 202	1 190				
1 177	1 169	1 170	1 168	1 170	Ring C–H i.p.b. (9a)
	982	984	984	986	$\nu O{-}CH_3$, $\nu O{-}C_2H_5$
932	930	932	938	934	$\nu\left(\mathrm{N}\begin{smallmatrix}\diagup\mathrm{C}\\ \diagdown\mathrm{C}\end{smallmatrix}\right)$
	688				
	532				Ring def. (9b)
	491		496		Ring def. (6a)
381	365				Ring δ(CNC)

[a] Formed by photolysis at 77 K. [b] Approximate description only, using Wilson notation.[11]

ν = Stretching, i.p.b. = in-plane bending, def. = deformation, δ = bending.

The problems of band assignments arise principally because of the uncertainty concerning the $N(CH_3)_2$ and *para*-substituent conformation in the molecules. It is not known whether the $C{-}N(CH_3)_2$ moiety is planar or non-planar with the benzene ring in either the parent or the radical form. This lack of structural information prevents the determination of the overall symmetry of the molecules and hence makes a full spectroscopic analysis very difficult. The resonance-enhanced bands of the radical are all thought to be totally symmetric (since depolarization ratios are 1/3). Using our previous results,[1] and those of others, the assignment of the ring vibration at *ca.* 1 600 cm^{-1} and the ring C–N stretching vibration[7] at *ca.* 1 400 cm^{-1} was quite straightforward, as was the assignment of the ring C–H in-plane bending mode at *ca.* 1 180 cm^{-1} (see Table 2). The most difficult assignments were those of the ring C–N stretching mode in the parent molecules and the band at *ca.* 1 520 cm^{-1} observed in all the radical cation spectra. The assignment of the former was made by reference to the work of Gates *et al.*,[10] which characterized the ring C–N stretching mode as lying between 1 300 and 1 350 cm^{-1} and giving a medium—strong band in the Raman spectrum. The band is also strongly polarized. The band at *ca.* 1 520 cm^{-1}, dependent on the overall symmetry of the system, is assigned to one of two possible ring modes: either 8(b) or 19(a) (using Wilson notation).[11] In the normal co-ordinate analysis of the TMPD parent and radical molecules [4] the ring 8(b) mode is assigned to bands at 1 565 and 1 511 cm^{-1}, respectively. The shift of -54 cm^{-1} is consistent with an increase in the quinonoid character of the radical cation. A negative parent-to-radical shift of a comparable magnitude (-61 cm^{-1}) was also calculated for the ring 8(b) mode in the 1,4-dimethoxybenzene system.[12] However, the 19(a) ring mode also usually occurs between 1 510 and 1 530 cm^{-1} for *para*-substituted benzenes.[13] This assignment has been used for a similar band observed for a series of donor–acceptor *para*-substituted *NN*-dimethylaniline radical cations in which a C_s point group symmetry has been assumed.[7] Therefore, the assignment of the *ca.* 1 520 cm^{-1} band remains ambiguous.

DISCUSSION

The photochemical production of the free radical cations studied here is thought to be a biphotonic process. The ionization potentials of the parent compounds are of the order of *ca.* 7.0 eV.[14] The u.v. lamp used to initiate photoionization had a maximum energy of 5.3 eV. The overall process has been verified as for the *para*-substituted anilines [1] and the optical absorption spectra have been used to characterize each of the radical cations.

The assignments (Table 2) of the radical cation bands, in particular that of the ring C–N stretching [ν(CN)] mode, clearly implies a greater quinonoid character in the radical than in the corresponding parent compound. The parent-to-radical shifts of +106, +57, and +58 cm^{-1} (see Table 3) for the DMPD, *p*-methoxy- and *p*-ethoxy-radicals, respectively, indicate corresponding increases in the ring C–N bond order. Smaller parent-to-radical shifts of +29 and +36 cm^{-1} were observed previously for the same mode in the *NN*-dimethyl-*p*-cyanoaniline [7] and TMPD systems,[4] respectively. An attempt to correlate these values with Hammett σ_p values reveals no obvious relationship (Table 3) although a correlation previously was found to exist for a similarly substituted series of anilines.[1]

TABLE 3

Comparison of ν(CN) bands (cm^{-1}) and the Hammett σ_p values [15] for *para*-substituted *NN*-dimethylaniline radical cations, $[(CH_3)_2NC_6H_4X]^+$

X	ν(CN) (parent)	ν(CN) (radical)	$\Delta\nu$(CN)	σ_p
$N(CH_3)_2$ [2,3]	1 340	1 376	36	-0.83
NH_2	1 309	1 415	106	-0.66
OCH_3	1 336	1 393	57	-0.268
OC_2H_5	1 338	1 396	58	-0.24
CN [6]	1 373	1 402	29	$+0.66$

The ν(CN) modes in the radical form for both series of radical cations studied [1] lie at approximately the same wavenumbers, *i.e. ca.* 1 400 cm^{-1}. In the *para*-substituted aniline parent compounds the ν(CN) mode occurs at *ca.* 1 270 cm^{-1}, whereas ν(CN) for the *NN*-dimethylaniline parent occurs between 1 309 and 1 338 cm^{-1}. It is thought that the differences in the parent ν(CN) frequencies may arise, in part, from differing geometries around the nitrogen atom. These differences may, in turn, account for the lack of correlation between the Δν(CN) and the Hammett σ_p values observed for this series of radical cations.

It is well established that aniline itself is non-planar.[16] For *NN*-dimethylaniline the case is not so clear. Some workers have suggested that the $N(CH_3)_2$ group is coplanar with the ring,[17] whilst others suggest it is non-coplanar.[18] In any event, it is probable [10] that the $N(CH_3)_2$ group is closer to a planar configuration than the NH_2 group. The fact that the NH_2 group for *para*-substituted parent compounds is not coplanar with the ring has been established by both *X*-ray crystallographic data and the large dipole moment of *p*-phenylenediamine. *X*-Ray crystallographic studies of *NN*-dimethyl-*p*-nitroaniline [19] have shown the $N(CH_3)_2$ group to be nearly coplanar with the ring. When this structure was compared with that of *p*-nitroaniline it was suggested that there was a greater contribution to a quinonoid form from the *NN*-dimethyl derivative. It was thought that this arose mainly because of the greater electron releasing properties of $N(CH_3)_2$ compared with the NH_2 group.

It may be that there is a larger contribution from a quinonoid form in the series of *NN*-dimethylaniline parent compounds studied here (as compared with the *para*-substituted anilines studied previously). This may, in part, arise from the geometry of the $N(CH_3)_2$ moiety and also partly from the electron-donating effect of the methyl groups. However, these effects may not be uniform throughout the series of compounds studied here and hence may account in part for the lack of correlation between the Δν(CN) data and the Hammett σ_p values.

Another factor that may affect this type of correlation is the amount of coupling that occurs between ring vibrations. The ν(CN) vibration is not a pure mode, but it is coupled to other molecular vibrations. The degree of mixing for these molecules is unknown. However, the previous vibrational studies of *p*-*NN*-dimethylaminobenzonitrile [10] and TMPD [4] showed that the so-called ν(CN) modes have only 23 and 37%, respectively, of ring C–N stretching character. In the radical form of TMPD [4] the corresponding mode involves only 26% ring C–N stretching character. The degree of mixing is not necessarily uniform throughout the series of *para*-substituted *NN*-dimethylaniline parents and radicals studied here. Thus differing amounts of mode mixing also could account for a poor correlation between Δν(CN) and σ_p values.

The excitation profiles for these radicals are shown together with their optical absorption spectra in Figure 1. The Raman spectra were all obtained from ethanol solutions. The resonance Raman spectra of the *p*-methoxy-*NN*-dimethylaniline radical cation are shown in Figure 2, as an illustrative example, using 568.2, 530.9, 514.5, 488.0, and 457.9 nm excitations. The intensities, I_j, of the more intense Raman bands were measured relative to that, I_{st}, of the 886 cm^{-1} band of the ethanol solvent. These values, I_j/I_{st}, were corrected at each excitation wavelength for spectral sensitivity of the instrument, the ν^4 factor, and self-absorbance by the radical cation. The excitation profiles plotted show the dependence on the excitation wavelength for each of the radicals studied. As can be seen [Figure 1(C)], the profiles drawn for the 1 637, 1 415, and 1 202 cm^{-1} Raman bands of the DMPD radical all maximized when 568.2 nm excitation was used. This implies that the resonance Raman effect, for these modes, is associated with the longest wavelength ($\lambda_{max.}$ *ca.* 570 nm) band of the electronic absorption spectrum. This is also the case for the other enhanced Raman bands which also maximized when 568.2 nm excitation was used (not drawn).

The *p*-methoxy- and *p*-ethoxy-*NN*-dimethylaniline radical cations show similar absorption spectra and excitation profiles [see Figures 1(A) and (B)]. All the profiles drawn (three for each system are given as examples) maximize at *ca.* 500 nm (as do the others—not drawn). Very little can be made of these data since no detailed molecular orbital treatment for any of these radicals can be found. It has been difficult to make inferences concerning the vibrational modes that most efficiently couple the ground and excited electronic states, and thus the nature of the excited state geometries for these radicals, in the absence of any strikingly enhanced Raman bands. No very profound conclusions can be drawn from the excitation profile data presented here.

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