Resonance Raman Spectrum of the *p*-Phenylenediamine Radical Cation

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Summary The Raman spectrum of the free radical formed by oxidation of *p*-phenylenediamine in solution has been obtained by the method of resonance enhancement; this radical spectrum is shown to differ substantially from that of the parent compound and some preliminary assignments are reported.

THE inherent reactivity commonly associated with free radicals results, in most situations, in low standing concentrations of radical species. The sensitivity of the normal vibrational Raman spectroscopic technique is insufficient for this to be a useful method of detecting and characterising such species. However, it has been amply demonstrated[1–3] that a large increase in some vibrational band intensities ensues when the light frequency used for exciting the spectra is coincident or close to coincidence with the frequency associated with a vibronic transition of the system; such is the resonance Raman effect (r.r.e.). Good quality r.r.e. spectra have been reported from low pressure gases and from solution phase species at 10^{-5}M and lower concentrations.[2–4]

We report here the r.r.e. spectrum obtained from the *p*-phenylenediamine radical cation in methanol at concentrations of the order of 10^{-4}M. This solution is yellow, having intense visible absorption band maxima at 463 and 490 nm. Excitation of the Raman spectrum with the 488 nm line of an argon ion laser satisfies the condition for resonance enhancement of the radical spectrum. Moreover, this enhancement occurs selectively in the presence of non-absorbing species and effectively minimises solvent interferences. This selectivity to the absorbing species gives r.r.e. an obvious advantage over i.r. spectroscopy for the study of vibrational modes of free radicals in solution.[5]

The radical cation was prepared by molecular bromine oxidation of a solution in methanol of *p*-phenylenediamine-dihydrochloride[6] (*ca.* 10^{-2}M). Its r.r.e. spectrum was

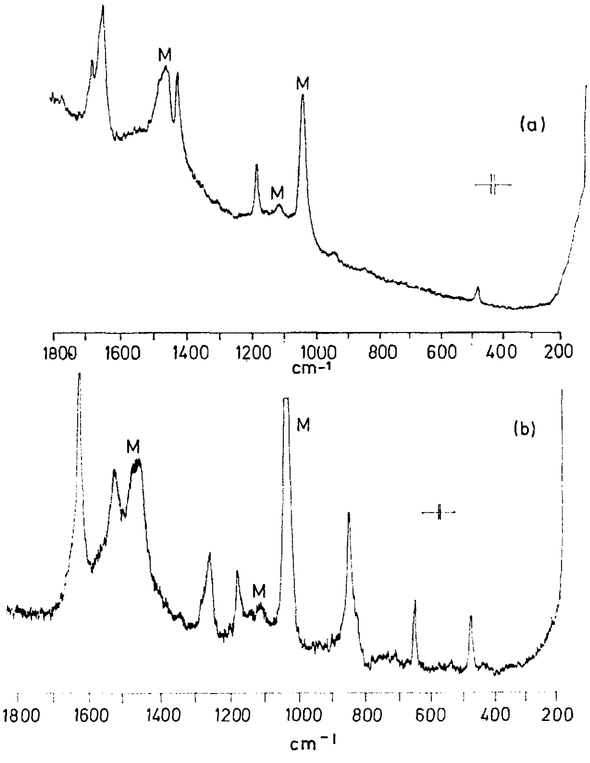
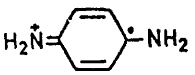
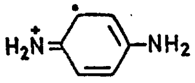


FIGURE. (a) *Resonance Raman spectrum of the free radical cation of* p-*phenylenediamine* (ca. 10^{-4}M) *in methanol.* (b) *Normal Raman spectrum of* p-*phenylenediamine* (ca. 1·0M) *in methanol. Spectrum* (a) *was excited by the* 488 nm *line of an argon ion laser in order to obtain maximum resonance enhancement, but spectrum* (b) *was excited by the* 514·5 nm *line to minimise problems of absorption by small coloured oxidation product impurities. Solvent bands are marked* M.

obtained using the rotating-cell technique[2] and is shown in the Figure over the interval 0—1800 cm^{-1} together with the normal Raman spectrum of the parent compound. The solution yielding the radical spectrum shown contained *ca.* 10^{-4}M radical concentration, estimated from the intensity of its visible absorption.[6] The excess (*ca.* 10^{-2}M) concentration of *p*-phenylenediaminedihydrochloride gave no detectable spectrum under the instrumental conditions used. As is evident from a comparison with methanol bands shown in the Figure, an approximate enhancement factor of 10^5 was achieved with the radical spectrum.


(1)


(2)

Striking differences between the spectra of *p*-phenylenediamine and its radical anion are readily apparent from the Figure. Band assignments may be made for the parent compound by comparison with the extensive and well-documented studies of related *p*-disubstituted benzenes,[7-9] studies which include a detailed normal co-ordinate analysis,[10] and measured band depolarisation ratios are useful in this. Since it is well established that not all vibrational band intensities are enhanced in the r.r.e., little chemical significance can be attached to the absence or reduced relative intensity of corresponding bands in the radical spectrum but, conversely, the appearance of bands in the radical spectrum which are absent from the spectrum of the parent compound is of great significance. On this basis the polarised band at 1418 cm^{-1} arising from the radical is particularly noteworthy. A reasonable interpretation of this is that it appears to correspond with the polarised band of *p*-phenylenediamine at 1257 cm^{-1}, this latter being due to a symmetric mode involving a large contribution from C–N stretching.[8,10] This interpretation implies a radical cation structure with partial double-bond character in the C–N bonds, most simply expressed by the canonical forms (**1**) and (**2**).

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