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Solvent Effects on the Coexistence of Localized and Delocalized 4,4′-Dinitrotolane Radical Anion by Resonance Raman Spectroscopy

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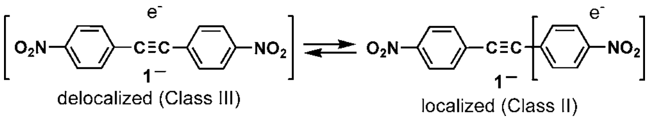
Dinitroaromatic radical anions were the first compounds (in the period 1960−1970)[1] for which intramolecular electron transfer was studied, using electron paramagnetic resonance spectroscopy, before the concept of mixed valency had been introduced by inorganic chemists.[2] After it was realized that these compounds are in fact all-organic mixed-valence (MV) compounds, it was argued that the narrow optical bands containing vibrational fine structure shown by 4,4′-dinitrotolane ($\mathbf{1}^-$)[3] in solvents that induce a low solvent reorganization energy (λ_s) for radical anions, as well as for those of most other dinitroaromatic radical anions in all solvents,[4] show that they are delocalized (class III in the Robin−Day classification).[2a]

More recently, solvents that induce a higher λ_s for $\mathbf{1}^-$ and related compounds have been shown to cause the gradual replacement of the narrow optical bands by the broad Hush-type charge-transfer bands of charge-localized MV compounds (class II), making it appear that class-II and class-III compounds might coexist in the same solutions (see Scheme 1).[3,5] Coexistence of localized and delocalized MV states of the same molecule in solution has rarely been observed. The equilibrium between the two species shifted from predominantly class III to predominantly class II as the solvent reorganization energy (λ_s) was increased. The optical spectra of $\mathbf{1}^-$,[2] among other dinitroaromatic radical anions, showed narrow bands having partially resolved vibrational fine structure typical of some class-III MV species in tetrahydrofuran (THF), a solvent that induces a low λ_s for radical anions, but showed a broad, nearly Gaussian-shaped band typical of charge-localized MV molecules in high λ_s solvents such as acetonitrile (MeCN).[3] In intermediate-λ_s solvents such as *N*,*N*-dimethylformamide (DMF), a superposition of these two kinds of absorption spectra was observed, and the relative amounts of the localized and delocalized bands in the optical spectra changed gradually with the solvent [Figure 1; spectra of $\mathbf{1}^-$ in a series of eight solvents can be found in Figure S1 in the Supporting Information (SI)].

Scheme 1



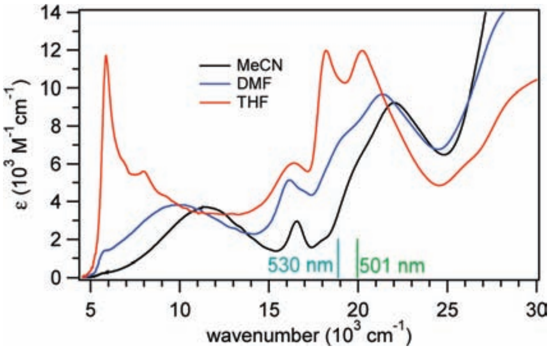


Figure 1. Optical spectrum of $\mathbf{1}^-$ in the three solvents used in this work. The band at 16500 cm^{-1} belongs to the dianion ($\mathbf{1}^{2-}$). The wavelengths of Raman irradiation are shown as sticks.

In this work, we studied the coexistence of localized and delocalized dinitro MV radical anions using the more structurally revealing resonance Raman (rR) spectra of $\mathbf{1}^-$. The alkyne bridge (C≡C) stretching frequency is diagnostic because the singly occupied molecular orbital (MO) of the bridge has antibonding character, causing a shift to lower frequencies when more electron density is delocalized onto the bridge. In addition, the $-$PhNO$_2$ charge-bearing units exhibit an intense ring-centered C═C stretch that shifts to higher frequency as charge is delocalized away from these units. These bands were used to characterize the anions.

Solutions of compound **1** were reduced to the radical anion $\mathbf{1}^-$ and subsequently to the dianion ($\mathbf{1}^{2-}$) using sodium amalgam in the presence of [2.2.2]cryptand in a closed Schlenk line tube. The optical spectra of the three species in MeCN are shown in Figure S2. The rR spectrum of $\mathbf{1}^-$ in solution contains two bands assigned to the alkyne stretch of the C≡C bridge at 2146 and 2166 cm^{-1}, but only one alkyne vibration should be present. The neutral and dianion oxidation states

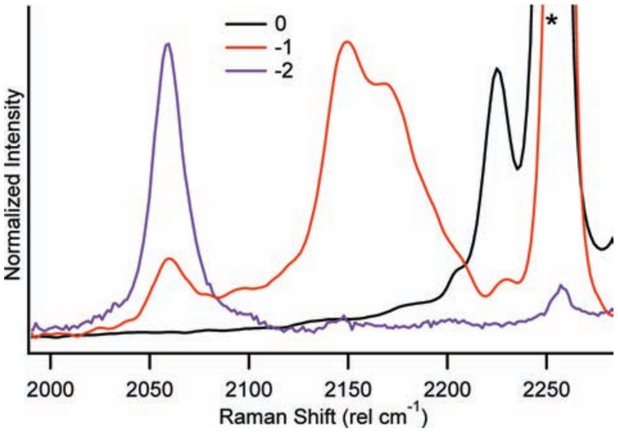


Figure 2. Raman spectra of $\mathbf{1}^0$, $\mathbf{1}^-$, and $\mathbf{1}^{2-}$ in MeCN, shown in black (collected at 482 nm), red (530 nm), and blue (530 nm), respectively. The intensity is arbitrary; solvent peaks are denoted by the asterisk.

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Table 1. Experimental and Calculated Raman Vibration Frequencies (cm^{-1}) for $\mathbf{1}^-$ in the 1000−2400 cm^{-1} Region

exptl values			calcd values[c]		
NB[a]	$\mathbf{1}^{0}$ [b]	$\mathbf{1}^{-}$ [b]	delocalized $\mathbf{1}^-$	localized $\mathbf{1}^-$ [d]	assignment[e]
−	2224	2166, 2146	2175	2207	C≡C stretch
−	−	1592	1621	1619	out-of-phase ring quinoid C≡C stretch
1586	1590	1570	1605	1605	in-phase ring quinoid C≡C stretch
−	1442	1445	1468	1419, 1456 (−)	molecular stretch and ring breathing
1346	1348	1330	1335	1356, 1380 (−)	C−N and N−O stretches and O−N−O bend
−	−	1266	1280	1302	M−C≡C−M bend
1163	1175	1176	1182	1197, 1167 (−)	C−H in-plane wag
−	1137	1137	1144	1137	M−(C≡C) stretch
1108	1105	1104, 1046	1093	1106, 1070 (−)	N−O and C−N stretches and ring breathing
1005	1010	1009	992	1013, 980 (−)	ring deformation

[a] Neat nitrobenzene; data from ref 13. [b] In MeCN. [c] The calculated results have been multiplied by an empirical correction factor of 0.98. [d] In cases where two values from the localized calculation are given, (−) denotes the vibration centered on the charged ring, and the other vibration is centered on the ring without the charge. When only a single value from the localized calculation is given, the vibration is shared on both the charged and neutral rings. [e] The charge-bearing nitrobenzene unit is abbreviated as M.

show significantly different stretching vibrations at 2224 and 2060 cm^{-1}, respectively (Figure 2). It should be noted that small amounts of the neutral and dianion species formed by disproportionation are present in both the optical and rR spectra of $\mathbf{1}^-$.

The presence of two peaks in the spectra of $\mathbf{1}^-$ indicates that there are two different molecules with slightly different solvent-stabilized geometries; on the basis of the previous absorption studies, the two species are assigned as the delocalized and localized tolane anions. The delocalized species has a lower frequency than the localized species because the singly occupied bridge MO has more electron density in its antibonding orbital. Not surprisingly, density functional theory (DFT)-calculated results using the UB3LYP method with various basis sets predicted a delocalized structure.[6] The localized structure was calculated using recently developed constrained DFT methods;[7] these calculations reaffirmed the assignment that the alkyne vibration of the localized species is higher in energy than that of the delocalized species (Table 1).

The DFT calculations were performed at the B3LYP/6-31G(d) level with the Q-Chem software package,[8] using a developers' version containing the implementation of constrained DFT. The charge-delocalized structure was obtained using B3LYP without any constraints. The charge-localized structure was calculated by constraining one $C_6H_4NO_2$ group to have one extra electron using the real-space weighting functions of Becke.[9,10] Both structures were fully optimized. The Raman spectra were computed at the optimized structures using finite-field numerical differentiation of analytical energy gradients.[11] The coordinates of the optimized geometries are given in the SI.

It was also experimentally observed that as the solvent was changed from THF to MeCN (increasing λ_s), the intensity of the high-energy peak increased relative to that of the low-energy peak (Figure 3), supporting the assignment that the high-energy peak arises from the localized form and the low-energy peak from the delocalized form. These interpretations are also consistent with optical absorption studies.

The relative intensities of the two alkyne vibrations differed as the wavelength was changed as a result of the changing amount of resonance enhancement. This is seen in Figures 2 and 3, where the relative enhancement of the localized species is greater in Figure 3 as the excitation wavelength is more in resonance with the localized species (Figure 1). The absorption spectrum directly reflects the relative concentrations of the two species; in THF, the delocalized species is the dominant species and shows the vibronic progression of the alkyne species, but in MeCN, the dominant species is the localized species, although some delocalized species is present in solution (Figure S3). The intensities in the rR spectra of $\mathbf{1}^-$ in MeCN reflect the Raman cross section of the two species; the delocalized species has a much higher Raman cross section than the localized species. The intensities reflect the relative concentrations as well as the Raman cross sections, which is a function of the amount of resonance enhancement.

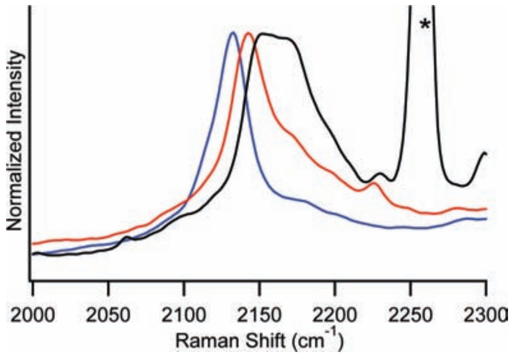

Figure 3. rR spectra (excited at 501 nm) of $\mathbf{1}^-$ in THF, DMF, and MeCN from left to right (blue, red, and black, respectively). Solvent peaks are indicated by the asterisk; the intensities have been normalized.

The strong C═C stretching mode that primarily involves the phenyl rings was also useful for verifying the coexistence of the two MV species. The resolved peaks at 1570 and 1592 cm^{-1} are assigned as quinoid-like ring stretches on the charge-bearing nitrobenzene units of $\mathbf{1}^-$ (Figure 4). The rR spectra of the $\mathbf{1}^0$ and $\mathbf{1}^{2-}$ oxidation states show single peaks at 1591 and 1519 cm^{-1}, respectively, and as the molecule is reduced, the vibrational frequency of these modes decreases. In the nitrobenzene monoanion,[12] difference spectra show a large decrease in the frequency of this mode (1475 cm^{-1} in the anion vs 1589 cm^{-1} in the neutral molecule).[13] The presence of two resolved peaks in the rR spectra of $\mathbf{1}^-$ is consistent with the coexistence of two species in solution. The interpretation of these peaks is more complex than in the case of the C≡C stretch because a total of four normal modes (in-phase and out-of-phase combinations of the displacements shown in Figure 3) for each of the localized and delocalized molecules is possible. The rR intensity interpretations are complicated by the presence of an overlapping high-energy absorption band (Figure 1).[14] The out-of-phase combination is not strongly resonance-enhanced in the delocalized molecules ($\mathbf{1}^0$ and $\mathbf{1}^{2-}$) but is more prominent in the localized system. The 1592 cm^{-1} mode is assigned as the out-of-phase ring quinoid stretch arising from the localized species. The 1570 cm^{-1} mode is assigned as the in-phase ring quinoid stretch, which gains intensity from both species, as the calculated values for the two species are the same for this vibration.

The remaining portion of the resonance Raman spectrum (Figure S4) shows intense peaks between 1000 and 1700 cm^{-1} that arise from the coupled charge-bearing nitrobenzene units (denoted as M); lower-energy vibrations were not considered because they were too weak to afford reliable information. $\mathbf{1}^0$ shows five Raman peaks that directly

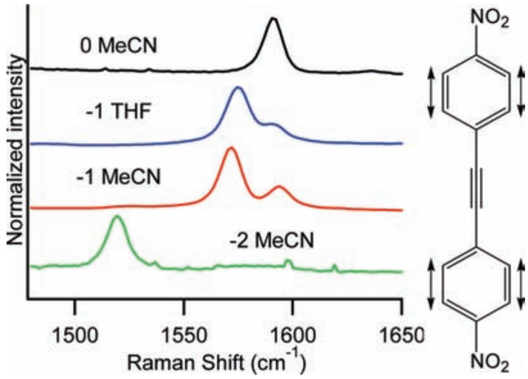

Figure 4. Raman vibrational bands of $\mathbf{1}^0$, $\mathbf{1}^-$, and $\mathbf{1}^{2-}$ excited at 482, 501, and 530 nm, respectively. The intensities of the most intense peaks have been normalized. The largest displacement vectors are depicted at the right.

correspond to peaks of neat neutral nitrobenzene and have the same assignments[13] (Table 1). Two additional vibrations present at 1137 and 1442 cm^{-1} are calculated to have significant M−(C≡C) stretching contributions.

Upon reduction to $\mathbf{1}^-$, a new peak at 1046 cm^{-1} appeared, and it is assigned as belonging to the localized species. The corresponding vibration in the delocalized species occurs at 1104 cm^{-1}; together they form another pair of vibrations that supports the hypothesis of solvent-mediated speciation. Calculations predicted a significant decrease in the frequency of this mode upon localization (1070 cm^{-1} vs 1093 cm^{-1} for the delocalized species), and there were no other available vibrations for assignment predicted at this energy.

The 1266 cm^{-1} peak is assigned as the M−C≡C−M bending mode, which would be more enhanced in the localized species than the delocalized species; this peak thus suggests the presence of a localized species. The calculated results for the nitro vibration at 1330 cm^{-1} for $\mathbf{1}^-$ suggest that the localized species should have a significant difference in frequency for the charged and neutral rings. The nitro vibration occurring at 1330 cm^{-1} in $\mathbf{1}^-$ was very broad, indicating the possibility of two closely overlapping peaks, but no distinguishable fine structure was observed.

The solvent reorganization energy λ_s can be changed not only by varying the solvent as discussed above but also by changing the temperature. The rR spectra of $\mathbf{1}^-$ in MeCN at three temperatures are shown in Figure 5. The intensity of the C≡C stretching band from the localized molecule increases relative to that of the delocalized band as the temperature is lowered, consistent with an increase in λ_s as the temperature is lowered. This trend is opposite to that predicted by the dielectric continuum theory.[15] These incorrect predictions occur for bishydrazine radical cations as well.[16] The dielectric continuum theory treats the solvent as a bulk material with a dielectric constant particular to the polarity of the solvent; it is satisfying in that it allows the solute and solvent to interact through paired opposing dipoles and presents a simple qualitative description.[17] It correctly predicted the trends reported in studies of pyrazine-bridged MV triruthenium clusters: as the temperature decreased and the solvent was frozen, the electron-transfer rate across the molecule increased and the molecule changed from class II to class III. The shift to class III was attributed to the decoupling of solvent modes on the electron transfer between the triruthenium clusters across the bridge as the solvent was cooled and eventually frozen.[18]

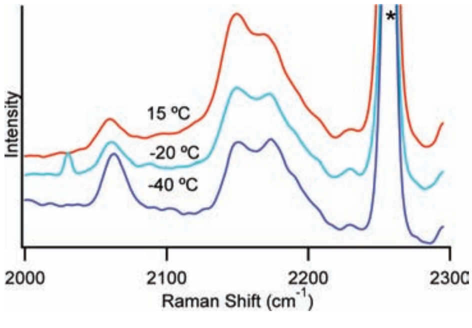

Figure 5. rR spectra (excited at 530 nm) of the C≡C stretching region of $\mathbf{1}^-$ in MeCN as a function of temperature.

A statistical theory formulated by Matyushov[19] has been reported that predicts an increase in λ_s as the temperature is lowered. The theory predicts that there will be regions of long-range order with aligned solvent dipoles, giving rise to the localized species in solution. The rest of the solvent has randomly oriented dipoles with no long-range interaction and acts as a “bulk” solvent, giving rise to the delocalized species. The theory treats the solvent molecules “independently” by considering the fluctuations of the solvent dipoles and density (commonly known as the fluctuation dissipation theorem). It is difficult to experimentally measure the parameters of the theory or to predict the solvents and MV molecules to which it best applies.[19]

In summary, the Raman spectrum of the simple alkyne bridge in $\mathbf{1}^-$ shows two distinct bands, providing proof of the solvent-dependent coexistence of two electronic species. The Raman spectra of normal modes primarily involving the charge bearing −PhNO$_2$ units also support the coexistence of two solvent-dependent electronic species. The temperature dependence of the spectra of the bridging unit shows an inverse relationship between λ_s and temperature, in agreement with the statistical theory.

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Supporting Information Available: Experimental details, optical and rR spectra, geometry-optimized coordinates of $\mathbf{1}^-$, and complete ref 8. This material is available free of charge via the Internet at http://pubs.acs.org.

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