

Raman Characterization of Phenyl-Derivatives: From Primary Amine to Diazonium Salts

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Abstract

The objective of the present work is to use Raman spectroscopy for characterizing the fate of phenyl-derivatives, from phenyl-amines to aryl-diazonium derivatives (ADD). Four ADD were investigated: (i) benzene diazoniumtetrafluoroborate (DS), (ii) 4-decyl benzene diazoniumtetrafluoroborate (DS-C₁₀H₂₁), (iii) 4-carboxybenzene diazoniumtetrafluoroborate (DS-COOH) and (iv) 4-(aminoethyl) benzene diazoniumtetrafluoroborate (DS-(CH₂)₂NH₂). Raman investigation of the above ADD confirmed the existence of an N≡N bond stretching in the range of 2285-2305 cm⁻¹. Moreover, the strong band related to CH in plane-bending and C-N-stretching modes in the 1073-1080 cm⁻¹ range, is a signature of phenyl derivatives stemming from ADD. Furthermore, we analyzed and discuss the H-N-(ring) symmetric stretching modes and the ring-N, as well as the benzene-ring vibrational modes, the C-H related vibrations and the functions in para-position carried by the aromatic ring. The effect of structural changes, the conformational rearrangements from amines to ADD and the influence of the substituent located in the para-position on Raman modes, were examined as well. Finally, Raman experiments supported by Density Functional Theory (DFT) modeling allowed us to determine the crystalline structure of DS-COOH.

Keywords: Phenyl-amines; Diazonium salts; Synthesis and characterization; Raman; DFT calculations

Abbreviations: ADD: Aryl-diazonium derivatives; DS: Benzenediazoniumtetrafluoroborate; DS-COOH: 4-Carboxybenzene diazoniumtetrafluoroborate; DS-C₁₀H₂₁: 4-decyl benzenediazoniumtetrafluoroborate; DS-(CH₂)₂NH₂: 4-(aminoethyl) benzenediazoniumtetrafluoroborate; DFT: Density functional theory; NBO: Natural bond orbital.

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Introduction

Aryl-diazonium derivatives (ADD) are a class of highly useful reaction intermediates, or reagents. Their salts are generally obtained from the diazotization of aromatic amines in the presence of tetrafluoroboric acid, hexafluorophosphate or hexafluoroantimonate [1]. Aryl-diazonium salts are widely used in organic chemistry as reactants for different syntheses. For instance, the process of nitrogen elimination from diazonium cations is a fundamental stage of the Meerwein [2] and Sandmeyer [3,4] reactions. For both of these reactions, improving the yield

depends on the application of diazonium salts that effectively lose dinitrogen (N₂).

The rise in popularity of aryl-diazonium salts has further resulted from their efficiency in surface functionalization, where covalently attached coatings on (semi)-conducting materials bear a wide range of functional groups [5-14]. In addition, the grafting can be accomplished by either chemical (spontaneous grafting), electrochemical, or physical methods [5-12,15]. Surface

functionalization using diazonium salts has thus become one of the most powerful methods for coatings [8,13,14] through linking (bio)molecules [16,17], polymers [18-20] or nanoparticles [21]. The resulting high-performance materials show improved chemical and physical properties and find widespread application [22].

Whatever the diazonium salt application, identification of the molecular bonds is of great importance for investigating, improving and/or controlling reaction pathways. Raman has been selected as one of the most accurate spectroscopic techniques for determining specific vibrational modes and thus for identifying the molecular bonds and structures.

In this work, four ADD were synthesized and investigated:

- benzene diazoniumtetrafluoroborate (DS),
- 4-carboxybenzene diazoniumtetrafluoroborate (DS-COOH),
- 4-decyl benzene diazoniumtetrafluoroborate (DS-C₁₀H₂₁), and
- 4-(aminoethyl) benzene diazoniumtetrafluoroborate (DS-(CH₂)₂NH₂).

The choice of aryl-diazonium salts was further motivated by the development of robust "long-life" (bio) sensors, as they can be used for surface functionalization in order to provide accurate pre-concentration of (bio) organic compounds for sensitive and reproducible sensing. The physical and chemical properties of the salts related to their interaction ability are summarized hereafter. DS is the simplest salt; it was chosen as a reference and because of the availability of the aromatic cycle for π - π stacking. DS-C₁₀H₂₁ has a long non-polar alkyl chain, whose lipophilic and hydrophobic character serves to pre-concentrate non-polar molecules. DS-COOH and DS-(CH₂)₂NH₂ can both be used for coupling biomolecules, or for pre-concentrating polar molecules.

We used Raman spectroscopy for characterizing the fate of these four phenyl-derivatives, from phenyl-amine derivatives to ADD. Of particular interest are N=N group vibrations, H-N-(ring) symmetric stretching modes, ring-N as well as benzene-ring vibrational modes, C-H related vibrations, and para functions carried by the aromatic ring, all of which are analyzed and discussed. For some bands, we examined the effect of structural changes as well as of conformational rearrangements, from amine to diazonium salt. The influence of the substituent located in the para position is discussed, especially in terms of the nature and force of the substituent [the mesomeric effect (-M) provided by COOH as well as the inductive effect (-I) provided by NH₂ and CH₃ carried by CH₂CH₂NH₂ and C₁₀H₂₁ substituents]. The selection of these four ADD justifies why the mesomeric effect induced by electron-donating groups (+M) has not been investigated in the present work.

In addition, Density Functional Theory (DFT) calculations and Natural Bond Orbital (NBO) charges were performed for DS-COOH in order to conduct the band assignment and to strengthen Raman-spectra interpretation.

Materials and Methods

Reagents

The reagents used were sodium nitrite (NaNO₂), tetrafluoroboric acid (HBF₄), diethyl ether (>98%, ACS reagent), aniline, 4-dodecyl-aniline, 4-aminobenzoic acid, 4-(2-aminoethyl)-aniline, purchased from Sigma Aldrich Chimie S.a.r.l (St. Quentin Fallavier, 38297 France).

Synthesis and purification of diazonium salts

Diazonium salts were obtained by oxidation of the corresponding aryl-amine at 0°C and using sodium nitrite [7]. For the four different diazonium salts, 4 mmol of the corresponding amine were mixed with 2 mL of tetrafluoroboric acid dissolved in 7 mL of milli-Q water. The mixtures were then cooled in ice for 15 min (1 hour for that containing 4-dodecyl-aniline). Afterwards, a solution of 300 mg (600 mg for the mixture containing 4-dodecyl-aniline) of sodium nitrite dissolved in less than 1 mL of milli-Q water was added drop-by-drop. During the reaction the temperature was maintained at 0°C. After two hours of reaction (96 hours for the mixture containing 4-dodecyl-aniline), the mixture was filtered through 0.2 μ m cellulose ester filters (Whatman, France) and thoroughly washed with cold diethyl ether.

Diazonium salt purification consisted in dissolving the crude solid in a small amount of deionized water, followed by recrystallization in diethyl ether. The recrystallization procedure lasted for 48 hours at 6°C. Recrystallized diazonium salts were then filtered (0.2 μ m of cellulose ester filters, Whatman, France), dried and stored at -20°C.

Raman measurements

Raman measurements were recorded on pure chemicals (as powder unless otherwise stated) with a Labram HR800 Raman microspectrometer (HORIBA Jobin Yvon SAS, 59650 Villeneuve d'Ascq, France). For both amines and diazonium salts, a robust laser diode at 691 nm (Ondax) that is suitable for many Raman applications [23] was used to avoid molecular resonance. For diazonium salts and the 4-aminobenzoic acid, the scattered light was collected by a 100x objective with a numerical aperture (N.A.) of 0.9. For liquid compounds (aniline, 4-(2-aminoethyl) aniline and 4-dodecylaniline), a water immersion objective (100x, N.A.=1.0) was used. Spectral resolution was less than 2 cm⁻¹ and spectral calibration was performed daily via a silicon sample. All presented spectra were baseline corrected and normalized using the spectrometer software (LabSpec, HORIBA Jobin Yvon). Each spectrum was normalized to its maximum intensity. For calculations, spectra were normalized regarding the C=C stretching mode [24] observed between 1570 and 1611 cm⁻¹.

Nuclear Magnetic Resonance (NMR) measurements

Synthesized diazonium salts and their primary amines were also characterized by NMR measurements. Spectra were recorded using a Bruker Avance III 400 MHz instrument (Bruker UK Ltd, Coventry CV4 9GH, United Kingdom). The procedure, NMR

spectra and ^1H chemical shifts are presented in the Supporting Information. The structure of the salts as well as the indexation of protons is presented in **Scheme 1**. RMN spectra of both amines and diazonium salts are presented on **Figure S1** in Supporting Information.

Computational details

All calculations were carried out using the Gaussian 09 suite of programs [25] using the B3LYP exchange and correlation functional [26,27] along with the 6-311++G(d,p) basis set for all atoms. The structures were optimized without symmetry constraint (see Supporting Information). The vibrational wavenumbers and normal modes were calculated within their harmonic approximation. A scaling factor of 0.976 was chosen on the basis of previously published work [28].

Results and Discussion

Figures 1-4 compare Raman spectra obtained for A) primary amines and B) corresponding synthesized diazonium salts.

The wavenumbers of important peaks are reported in **Table 1** and their assignments were provided from the literature [24,29,30]. The spectrum obtained for aniline is in a good agreement with the one provided by Badawi [24]; most of their band assignments

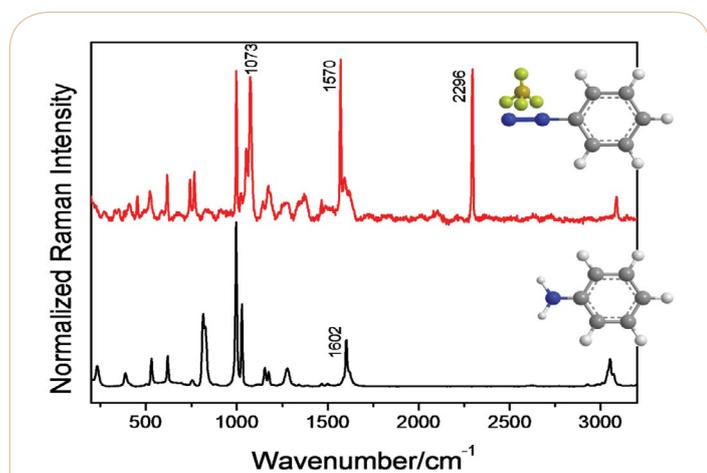
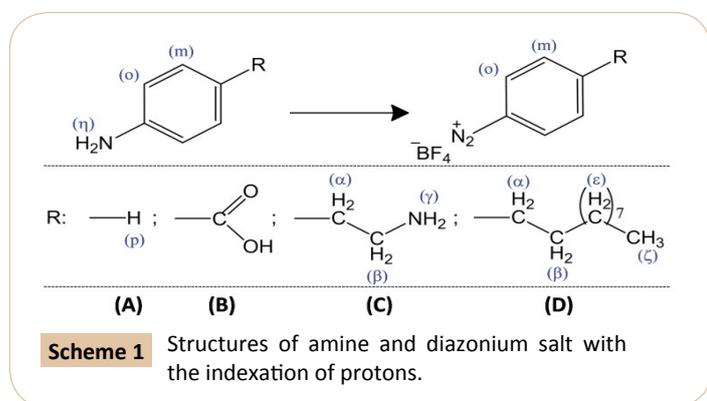


Figure 1 Raman spectra of aniline (black spectrum) and the corresponding diazonium salt benzene diazonium tetra fluoroborate, DS (red spectrum). Each spectrum was normalized to its maximum intensity.

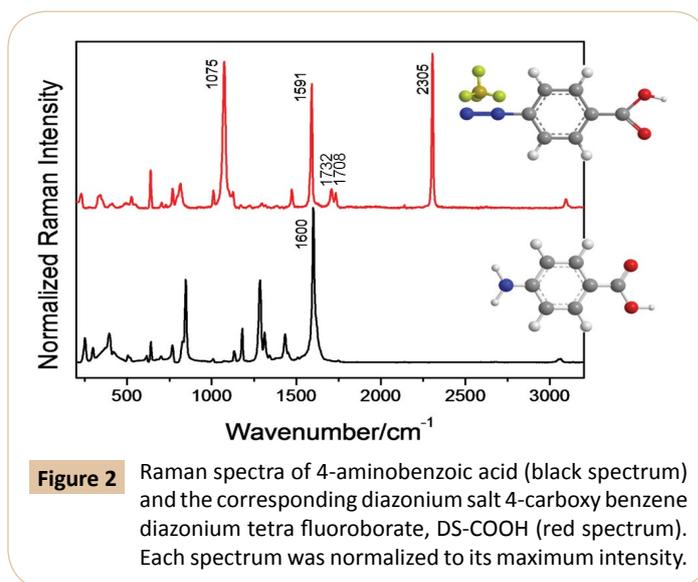


Figure 2 Raman spectra of 4-aminobenzoic acid (black spectrum) and the corresponding diazonium salt 4-carboxy benzene diazonium tetra fluoroborate, DS-COOH (red spectrum). Each spectrum was normalized to its maximum intensity.

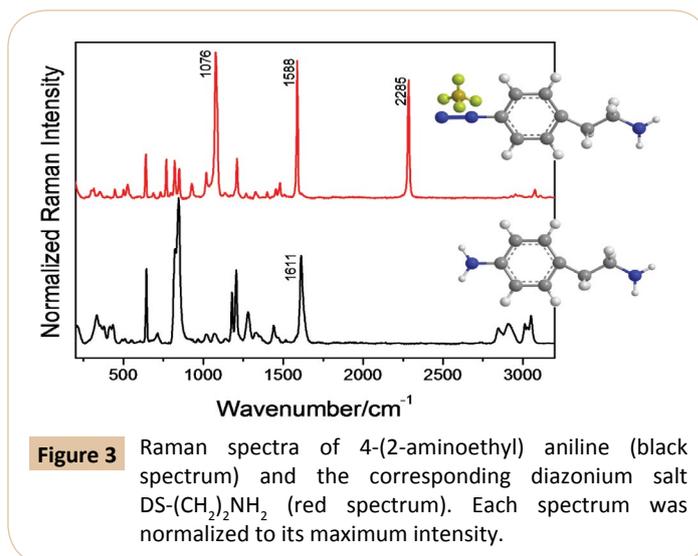


Figure 3 Raman spectra of 4-(2-aminoethyl) aniline (black spectrum) and the corresponding diazonium salt DS-(CH₂)₂NH₂ (red spectrum). Each spectrum was normalized to its maximum intensity.

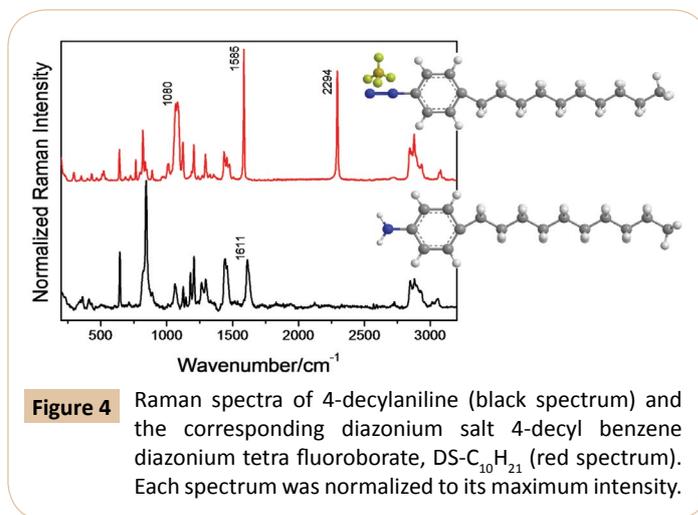


Figure 4 Raman spectra of 4-decylaniline (black spectrum) and the corresponding diazonium salt 4-decyl benzene diazonium tetra fluoroborate, DS-C₁₀H₂₁ (red spectrum). Each spectrum was normalized to its maximum intensity.

were used as reference for this work.

In addition, interactions can occur between two salts in a crystalline state, especially for DS-COOH because carboxyphenyl-

Table 1 Universal band assignments for Raman spectra obtained experimentally for primary amines and for the corresponding diazonium salts.

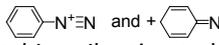
Raman wavenumber/cm ⁻¹								Assignment
Amines				DS				
Aniline	COOH	(CH ₂) ₂ NH ₂	C ₁₀ H ₂₁	DS	DS-COOH	DS-(CH ₂) ₂ NH ₂	DS-C ₁₀ H ₂₁	
386								Aromatic ring-N in plane bending [24]
619	638	643	644	617	637	640	639	Ring deformation [24]
755				743				p CH wagging [24,29]
814	828	822	822		796	820	819	o; m CH wagging [24,29]
827	845	845	844		814	849	837	Ring breathing [24]
995				997				Ring deformation + ring breathing for benzene and mono-substituted derivatives [24,29]
1027				1021				CC stretching vibration (coupled with CH in plane bending vibration) [30,31]
		1067	1062			1082	1079	C-C stretching (aliphatic chain) [29]
				1073	1075	1076	1080	CH in plane bending for p-substituted and mono-substituted benzenes [12,29] coupled with C-N stretching
1154				1142				m; p CH in plane bending [24,29]
1175	1179	1177	1179	1174	1170vw	1198vw	1190vw	m; o CH in plane bending [24,29]
1279	1286	1279	1265					Ring-N str + ring breathing + o-CH in plane bending [24]
		1469	1459			1454	1456	CH ₂ scissoring [32]
1602	1600	1611	1611	1570	1591	1588	1585	C=C stretching [24]
	1748				1708			C=O stretching
				2296	2305	2285	2294	N≡N stretching [24,29]
		2813-2986	2813-2986			2813-2986	2813-2986	Symmetric and antisymmetric CH stretch of n-alkanes [29]
3053-3071	3049-3063	3014-3051	3016-3057	3087	3096	3076	3066-3077	Aromatic CH stretch of benzene derivative [24,29]

derivatives are both H-bonding donor and acceptor. Thus, they preferentially self-organize as dimers in the crystalline state [33-35]. To investigate the dimer formation and obtain a clear assignment of the DS-COOH Raman bands, DFT calculations and Natural Bond Orbital (NBO) charges were carried out, examining two models. The first one considered monomer units (named CBN₂) whereas the second one considered DS-COOH dimers (named CBN₂ dimer). **Figure 5A** shows a comparison between the Raman spectrum for DS-COOH and the calculated vibrational features of the monomer (CBN₂) and the dimeric arrangement via H-bonds (CBN₂ dimer). The Raman band assignments of important peaks are shown on **Table 2**. The crystalline state of DS-COOH regarding the CBN₂ and CBN₂ dimer models is discussed over the presentation of the different investigated modes of phenyl-derivatives.

N≡N group vibrations

The particularity of diazonium salts is their N₂⁺ function obtained by oxidation of the corresponding amine. The strong peaks observed at 2296, 2305, 2285 and 2294 cm⁻¹ for DS, DS-COOH, DS-(CH₂)₂NH₂ and DS-C₁₀H₂₁, respectively, (**Figures 1-4; Table 1**) on the salt spectra compared to aniline ones, are due to the N≡N bond [12,29]. Compared to the experimental data acquired for each compound, the DFT calculations on DS-COOH revealed strong similarities in this spectral range (**Figure 5, Table 2**). The calculated position for the N≡N stretching mode was found at 2293 cm⁻¹ for CBN₂ and at 2304 cm⁻¹ for CBN₂ dimer. The similarity

between the latter theoretical position and the experimental one (the DS-COOH N≡N stretching mode is recorded at 2305 cm⁻¹) strengthens the fact that the best model for reproducing the vibrational features of the normal Raman spectra is a dimeric arrangement of the diazonium cation via H-bonds.

According to the literature [29,36], the position of the N≡N vibration mode depends upon the nature of the ring substituent located in the para-position of a diazonium salt. Our results show that substituents have a rather low effect on the N≡N fragment following the observed wavenumber shifts (**Table 1; Figure S2** in Supporting Information). For DS-COOH, however, the COOH electron-withdrawing tendency was confirmed by calculation of the C_{N≡N} NBO charges. Indeed, the C_{N≡N(DS-COOH)} NBO charge is equal to 0.012 compared to the C_{N≡N(DS)} NBO charge that is 0.003. As a result, a shift of +9 cm⁻¹ of the N≡N vibration mode was found for DS-COOH relative to DS. The electron-withdrawing groups (i.e., COOH) induce an increase of the contribution of a structure like  and hence induce a shift of the N≡N stretching vibration to higher wavenumbers [29,36]. This agrees with the N≡N bond-length decrease [36] and is also consistent with the polarizability increase of the N≡N bond. Experimental data show in fact that the relative intensity of the N≡N bond is increased by 23% for DS-COOH compared with that obtained for DS, DS-C₁₀H₂₁ and DS-CH₂CH₂NH₂ (**Figure S2** and **Table S1** in Supporting Information)

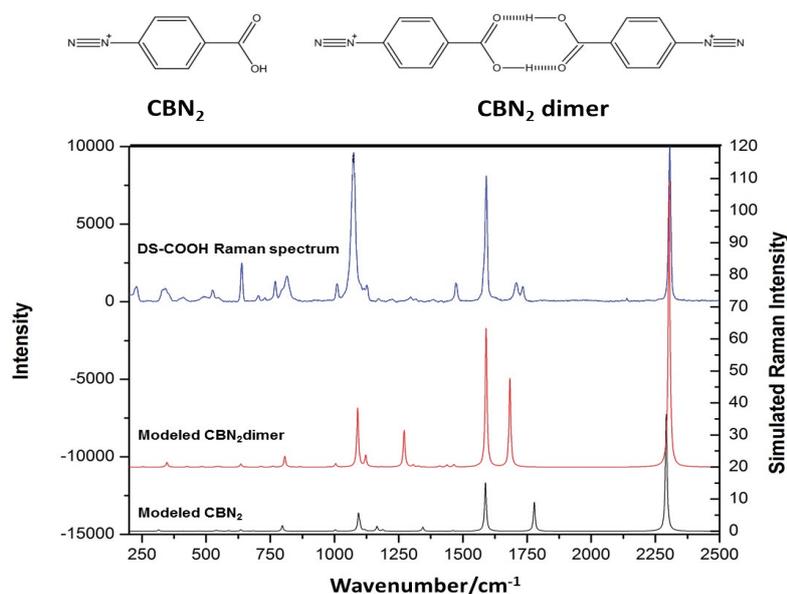


Figure 5 Comparison of the experimental Raman spectrum recorded for DS-COOH and the calculated vibrational features of the salt, by considering monomer (CBN_2) and dimeric arrangements via H-bonds (CBN_2 dimer).

Table 2 Comparison of experimental and calculated wavenumbers considering CBN_2 and CBN_2 dimer for modeling. Assignments of the main peaks. \times Calculated CBN_2 dimer features a center of symmetry imposing the mutual exclusion rule for vibrational modes. In this framework, the $\nu_{\text{sym}}(\text{C}=\text{O})$ is Raman active while $\nu_{\text{asym}}(\text{C}=\text{O})$ is Raman inactive.

DS-COOH	CBN_2		CBN_2 dimer	
Experimental/ cm^{-1}	Calculated/ cm^{-1}	Assignment	Calculated/ cm^{-1}	Assignment
2305	2293	$\nu(\text{N}\equiv\text{N})$	2304	$\nu(\text{N}\equiv\text{N})$
	1778	$\nu(\text{C}=\text{O})$		
1708			1684	$\nu_{\text{sym}}(\text{C}=\text{O})$
1732			\times	$\nu_{\text{asym}}(\text{C}=\text{O})$
1591	1588	$\nu(\text{C}=\text{C})$	1590	$\nu(\text{C}=\text{C})$
1293 wvw	1344	$\nu(\text{CO-H})$	1271	$\nu_{\text{sym}}(\text{CO-H})$
	1165	$\nu(\text{C-H})$ in plane and $\nu(\text{CO-H})$		
1127 ww			1122	$\nu(\text{C-H})$ in plane
1075	1093	$\nu(\text{C-H})$ in plane, $\nu(\text{C-N})$ and $\nu(\text{C-O})$	1090	$\nu(\text{C-H})$ in plane, $\nu_{\text{sym}}(\text{C-N})$
814	797	Ring breathing	807	Ring breathing

On the contrary, electron-donating groups located in para-positions induce an increase in the contribution of a structure like $\text{C}_6\text{H}_4\text{-N}^+\equiv\text{N}$ and $\text{C}_6\text{H}_4\text{-N}^+=\text{N}$ and, hence, a decrease of the $\text{N}\equiv\text{N}$ stretching vibration wavenumber. Such shifts are effectively observed in our experimental results since shifts of -11 cm^{-1} and -2 cm^{-1} of the $\text{N}\equiv\text{N}$ vibration mode were evaluated for $\text{DS}-(\text{CH}_2)_2\text{NH}_2$ and $\text{DS-C}_{10}\text{H}_{21}$, respectively, compared to that observed for DS. Of the two electron-donating groups CH_3 and NH_2 , NH_2 has the higher inductive effect [NH_2 substituent constants (σ_p) = -0.66 ; CH_3 substituent constants (σ_p) = -0.17] [37,38]. Moreover, the inductive effect drops off rapidly with the number of σ bonds. This is why:

(i) The negative shift in wavenumber observed for $\text{N}\equiv\text{N}$ vibration for $\text{DS-C}_{10}\text{H}_{21}$ is not significantly different from the one observed for DS, and why

(ii) The negative shift in wavenumber observed for $\text{N}\equiv\text{N}$ vibration of $\text{DS}-(\text{CH}_2)_2\text{NH}_2$ is higher than that observed for $\text{DS-C}_{10}\text{H}_{21}$.

H-N-(ring) symmetric stretching mode

In addition to the occurrence of an $\text{N}\equiv\text{N}$ stretching vibration, the N-H symmetric stretching disappears in the high wavenumber range $3250\text{-}3400 \text{ cm}^{-1}$ for primary amines (Figure 6). This indicates the successful synthesis of diazonium salts with a high production rate, which was confirmed by NMR study with the disappearance of the η band on the NMR spectra (Supporting Information). Each spectrum was normalized to its maximum intensity.

Ring-N vibrational modes

According to Badawi [24] and Wojciechowski [30], the peak at 386 cm^{-1} for the aniline molecule (Figure 1), corresponds to planar

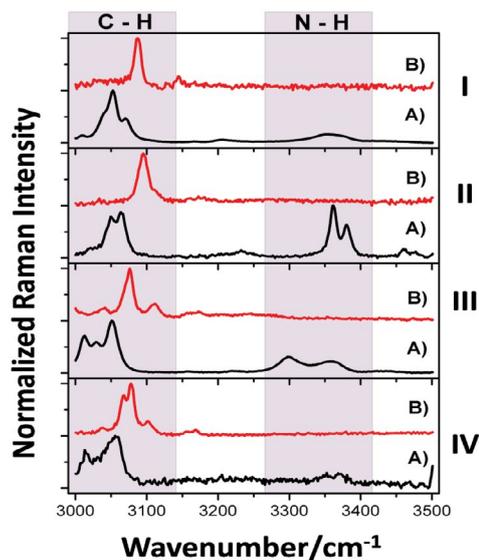


Figure 6 Comparison of aromatic C-H stretching and N-H stretching modes between the four synthesized diazonium salts (B red lines) and the corresponding primary amines (A black lines). Roman numbers I to IV correspond to DS, DS-COOH, DS-(CH₂)₂NH₂ and DS-C₁₀H₂₁, respectively.

bending of an aromatic ring-N. However, this vibrational mode is less obvious for para-substituted amines. A possible explanation is that aromatic-ring-vibration modes depend on the mass of the substituent [29]. Thus, in the range of 200-580 cm⁻¹, many vibrational modes can be observed depending on the nature of the para-substituted group (Figures 2-4). The same conclusion is valid for the range of 1250-1290 cm⁻¹, another range where a band corresponding to C-N vibration can be located. Raman bands for the amines observed between 1265 and 1279 cm⁻¹ (Table 1) and assigned to ring-N stretching coupled to ring breathing and to ortho-CH in plane bending [24], is no longer seen in the diazonium salt spectra.

This effect may be due to significant structural changes and conformational rearrangements, as the theoretical and experimental data provided by literature indicate that the neutral aniline in its ground electronic state (¹A₁) is non-planar. The dihedral angle between the NH₂ plane and the C₆H₅N plane was determined to be 37 ± 2°, assuming that the C-N bond makes an angle of 1.5-2.3° [30]. In comparison, the corresponding diazonium salt (aryl-diazonium) is a quasi-planar molecule [39], assuming that the C-N bond makes an angle of 0.5° [40]. The main factor causing this quasi-planarity is undoubtedly the strong through-bond interaction between the ring, which is known to be a strong electron donor, and the N₂ group, which is the strongest known electron acceptor [39]. In agreement with the literature [30,39,41], this bond lengthens so that co-planarity is maintained. An additional explanation could be related to the electron-charge density redistribution in the C-N bond. This is consistent with the observation that the diazonium group is one of the most powerful σ-electron and π-electron acceptors [41].

Benzene-ring and C-H related vibrations

By comparing Raman spectra from amines and diazonium salts, several common bands related to benzene-ring vibrations can be observed. First of all, a strong band related to the benzene-ring stretching mode (Table 1) occurs on all Raman spectra in the range of 1585-1611 cm⁻¹. According to Wojciechowski [30], this band is essentially related to ortho-meta C-C stretching modes. From phenyl-amine derivatives to diazonium salts, this band is the most significant signature of the benzene ring. Compared to the primary amines, this band is shifted to a lower wavenumber for all salts. These shifts are close to 25 cm⁻¹ for salts except DS-COOH, maybe due to the higher weight of the N₂ group compared to NH₂ that induces a decrease of the vibration frequency. In the case of DS-COOH, the shift of less than 10 cm⁻¹ may be due to the dimeric form of the salt that reduces the weight effect of the N₂.

Two strong and distinct peaks again assigned to the ring-deformation and ring-breathing modes-coupled with CH in plane-bending vibration of benzene and of mono-substituted derivatives, are found in the Raman spectrum of aniline around 1000 cm⁻¹ (Figure 1; Table 1, trigonal ring breathing vibration) and 1027 cm⁻¹ (Figure 1; Table 1) [30,31]. For DS, these bands are slightly shifted to 997 and 1021 cm⁻¹. In case of para-substituted amines and diazonium salts (di-substituted benzene derivatives) these vibrational modes are not allowed [29].

Bands assigned to ring deformation (C=C-C in plane deformation) in the region of 617-644 cm⁻¹ (Table 1) are present for both amines and diazonium salts. In agreement with Socrates [29], the bands shift to a higher wavenumber for para-substituted aromatic compounds compared to mono-substituted compounds.

According to Badawi [24], the vibrational mode at 827 cm⁻¹ (Table 1) for aniline can be assigned to a ring-breathing mode, coupled with ring-N stretching and ring deformation. This band is shifted to higher wavenumbers (844-845 cm⁻¹) for para-substituted amines. However, shifts of -31 cm⁻¹ and -7 cm⁻¹ toward lower wavenumbers are observed for DS-COOH and DS-C₁₀H₂₁ respectively, compared to their primary amines, whereas in the Raman spectrum of DS-(CH₂)₂NH₂ a shift of +4 cm⁻¹ was found. In common for all substituted diazonium salts, the intensity of this vibrational mode strongly decreases and is no longer observed in the Raman spectrum of DS. Another vibrational mode at 814 cm⁻¹ assigned o,m-CH wagging (Table 1 and Figures 2-4) was found to behave in similar manner as described above for the ring-breathing mode. The shift of these bands may be due to structural changes and conformational rearrangements caused by the presence of the N₂⁺ [39,41].

Concerning the C-H ring related vibrations, bands assigned to p-CH wagging-coupled with ring-N wagging and o-CH wagging at 755 and 743 cm⁻¹ (Table 1) as well as m, p-CH bending-coupled with ring deformation at 1154 and 1142 cm⁻¹ (Table 1) are only observed for aniline and DS, due to mono-substitution.

The very strong band observed around 1075 cm⁻¹ and assigned to CH in plane bending-coupled with ring-N stretching mode for mono- and para-substituted benzenes in diazonium-salt spectra,

is of particular interest (red spectra on **Figures 1-4; Table 1**). The appearance of this band is an astonishing phenomenon, explained by electron-charge density redistribution within the structures caused by the presence of N_2^+ . It is also the indisputable signature of phenyl-derivatives stemming from diazonium salts.

According to the literature, aromatic C-H symmetric and antisymmetric stretching modes occur above 3000 cm^{-1} and show a multiplicity of weak to moderate bands [42]. In comparison with amines, CH stretching (**Table 1**) shifts toward the higher wavenumber for diazonium salts (**Figure 6**). This shift indicates a strengthening of the C-H bond, possibly due to a new charge distribution on the ring after the substitution of NH_2 by N_2^+ [30]. This result is in good agreement with the ones in the literature for aniline and its corresponding diazonium salt [30,39,41].

Functions in para- position carried by the aromatic ring

Concerning the different functions in para-position carried by the aromatic ring ($COOH$, $(CH_2)_2NH_2$ and $C_{10}H_{21}$), some characteristic bands have been identified. For $(CH_2)_2NH_2$, $C_{10}H_{21}$ and their corresponding diazonium salts, symmetric and antisymmetric CH_3 stretches of n-alkanes as well as symmetric CH_2 stretches of n-alkanes are clearly identified in the range of $2813\text{-}2986\text{ cm}^{-1}$ (**Figures 3 and 4; Table 1**). In addition, C-C stretching mode occurs in the range of $1062\text{-}1082\text{ cm}^{-1}$ (**Table 1**) and CH_2 scissoring in the range of $1454\text{-}1469\text{ cm}^{-1}$ (**Table 1**). Some significant changes in peak position or intensity occur, meaning that the simple modification of the molecule from aniline form to diazonium salt could have a strong influence on the vibrational modes of the alkyl chain in para-position.

Concerning aminobenzoic acid derivatives (**Figure 2; Table 1**), the weak bands in the $1700\text{-}1750\text{ cm}^{-1}$ region are characteristic features of the carboxylic group due to C=O stretching vibration. They were respectively assigned to symmetric and antisymmetric stretching vibrations at 1708 and 1732 cm^{-1} . The antisymmetric stretch is usually seen at a higher wavenumber than the symmetric one [43]. With regards to DFT calculations (**Figure 5; Table 2**), the CBN_2 -model simulated spectrum predicts a single C=O stretching mode, $\nu(C=O)_{CBN_2}$, at 1778 cm^{-1} . This DFT numerical modeling is in good agreement with the literature [29]: when carbonyl does not interact with a hydrogen bond (the monomer case), the stretching bands appear in the range $1760\text{-}1735\text{ cm}^{-1}$. However, the dimer should be characterized by two C=O stretching modes, the symmetric C=O one ($\nu_{sym}(C=O)_{CBN_2\text{ dimer}}$) at 1683 cm^{-1} and the antisymmetric C=O one ($\nu_{asym}(C=O)_{CBN_2\text{ dimer}}$) at 1729 cm^{-1} . With regard to Raman calculations of the C=O stretching mode in the CBN_2 model ($\nu_{sym}(C=O)_{CBN_2}$ at 1778 cm^{-1}), the theoretical shift toward the lower wavelength of the symmetric C=O stretching mode in the dimer [$\nu_{sym}(C=O)_{CBN_2\text{ dimer}}$ at 1683 cm^{-1}] is due to a change in polarizability of the CO group induced by hydrogen bonding. The simulated Raman spectrum for CBN_2 dimer only shows this latter symmetric mode [$\nu_{sym}(C=O)_{CBN_2\text{ dimer}}$] at 1683 cm^{-1} . This concurs with the fact that the CBN_2 dimer features a center of symmetry imposing a mutual exclusion rule for vibrational modes. In this framework, the $\nu_{sym}(C=O)_{CBN_2\text{ dimer}}$ is Raman active,

while $\nu_{asym}(C=O)_{CBN_2\text{ dimer}}$ is Raman inactive. This mutual exclusion rule explains why the simulated Raman spectrum for an isolated CBN_2 dimer only shows symmetric C=O stretching.

However, the same dimer considered in the crystal packing has a lower symmetry that suspends the mutual exclusion rule, both $\nu_{sym}(C=O)_{CBN_2\text{ dimer}}$ and $\nu_{asym}(C=O)_{CBN_2\text{ dimer}}$ becoming Raman active. This is consistent with the two peaks on the experimental Raman spectrum of DS-COOH for both the symmetric and antisymmetric C=O stretching modes. The shift toward a higher wavenumber observed experimentally for symmetric C=O stretching from the theoretical $\nu_{sym}(C=O)_{CBN_2\text{ dimer}}$ value calculated at 1683 cm^{-1} to the experimentally measured $\nu_{sym}(C=O)_{DS-COOH}$ value at 1708 cm^{-1} is probably caused by the presence of BF_4^- in the crystalline structure of DS-COOH. This agrees with the effect provided by electronegative atoms, which increase the C=O stretching vibration wavenumber [44,45]. In addition to and in agreement with the results shown on **Table 2**, the similarities between the experimental and the theoretical position of $\nu(N=N)$, $\nu(C=C)$, ring breathing and $\nu(C-H)$ in plane, $\nu_{sym}(C-N)$, $\nu_{sym}(CO-H)$ as well as $\nu(C-H)$ in plane confirm the fact that the best model for reproducing the vibrational features of the normal Raman spectra is a dimeric arrangement of DS-COOH via H-bonds.

Conclusions

The work consisted in a Raman characterization of synthesized diazonium salts, comparing them with Raman spectra provided for amines. Raman investigation of synthesized diazonium salts confirmed the stretching of the $N=N$ bond in the expected spectral range of $2285\text{-}2305\text{ cm}^{-1}$ (2296 , 2285 , 2305 , and 2294 cm^{-1} for DS, DS-COOH, DS- $(CH_2)_2NH_2$ and DS- $C_{10}H_{21}$, respectively). The disappearance of the H-N-(ring) symmetric stretching observed in the range $3299\text{-}3361\text{ cm}^{-1}$ for the primary amines, is another evidence of the effectiveness of salt synthesis. Moreover, our results indicate that the very strong band related to the combination of both CH in-plane bending for mono- and para-substituted benzenes as well as C-N stretching in the range $1073\text{-}1080\text{ cm}^{-1}$, constitutes an actual spectral signature of the phenyl-derivatives stemming from diazonium salts.

Furthermore, the fate of phenyl-derivatives has also been examined by using Raman spectroscopy; this covered $N=N$ group vibrations, H-N-(ring) symmetric stretching modes, ring-N as well as benzene-ring vibrational modes, C-H-related vibrations and para functions carried by the aromatic ring. We especially considered both

- 1) The effect of structural changes and the conformational rearrangements from amine to diazonium salt, and
- 2) The influence of the substituent located in a para position, i.e., the nature and force of the mesomeric effect of the substituent, on the Raman modes.

Comparison between Raman experiments and DFT modeling showed that DS-COOH self-organized as dimers in the crystalline state.

This paper reports on a preliminary study designed as a lead-in to further examinations for investigating, improving and/or controlling reaction pathways using synthesized diazonium salt (i.e., to examine and strengthen the nature of the interface between Gold NanoStructures (GNS, electron-beam nano-lithographed SERS substrates) and organic coatings) [46].

Author Contributions

All authors have given approval to the final version of the manuscript. SB and IT contributed equally.

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