Experimental and Theoretical Insights into the Optical Properties and Intermolecular Interactions in Push-Pull Bromide Salts

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Experimental and theoretical insights into the nature of intermolecular interactions and their effect on optical properties of 1-allyl-4-(1-cyano-2-(4-dialkylaminophenyl)vinyl)pyridin-1-ium bromide salts (I and II) are reported. A comparison of optical properties in solution and in the solid-state of the salts (I and II) with their precursors (Ia and IIa) is made. The experimental absorption maxima ($\lambda_{\text{max}}$) in CHCl$_3$ is at 528 nm for I and at 542 nm for II, and a strong bathochromic shift of ~110 nm is observed for salts I and II compared with their precursors. The absorption bands in solid-state at ~627 nm for I and at ~615 nm for II that are assigned to charge transfer (CT) effect. The optical properties and single crystal structural features of I and II are explored by experimental and computational tools. The calculated $\lambda_{\text{max}}$ and the CT are in good agreement with the experimental results. The intermolecular interactions existing in the crystal structures and their energies are quantified for various dimers by PIXEL, QTAIM and DFT approaches. Three types of interactions, (i) the cation–cation interactions, (ii) cation–anion interactions and (iii) anion–anion interactions are observed. The cationic moiety is mainly destabilized by C–H···N/π and π···π interactions whereas the cation and anion moiety is predominantly stabilized by strong C–H···Br$^-$ interactions in both structures. The existence of charge transfer between cation and anion moieties in these structures is established through NBO analysis.

1. Introduction

Fluorescence dyes are widely used as fluorescence probes which are used in the chemistry, biology and physics for monitoring specific properties such as ON-OFF switches, ion sensing, explosive detection, luminescence-based bioimaging, etc. Luminescence property of the materials is sensitive to the external stimuli such as temperature, polarity, viscosity, pH and crystal packing. On the other hand, fluorescence probes based on the stilbazolium salts (D-$\pi$-A’ X) are used to monitor viscosity, pH, and photopolymerization reaction of methyl acrylates and other polymerization processes. The physical and spectroscopy studies on the quaternary salt (D-$\pi$-A’ $X^-$) have been reported by Fromherz’s[6] and Retting’s[7] research groups. Recently, Yu, et al. reported a (2-4-(1-cyano-2-(4-dimethylamino)phenyl)vinyl)(phenyl)-1-methylpyridin-1-ium hexafluorophosphate quaternary salt (Scheme 1, a), which is used as a luminescent imaging agent for mitochondria and nucleolus in living cells. The salt exhibits two different color emission in the mitochondria and cell nucleolus.[8] The (2-4-(1-cyano-2-(4-diphenylamino)phenyl)vinyl)(phenyl)-1-methylpyridin-1-ium hexafluorophosphate, (Scheme 1, b) has been reported as mitochondrion-targeted photosensitizing agents for the visualization of cancer cells.[8]

Last few decades, an impressive amount of attention has been devoted to the development of various organic D-$\pi$-A systems, because they have high polarizability and the strong intramolecular charge transfer (ICT) abilities. A typical push-pull organic D-$\pi$-A chromophore consists of strong electron donors (D) and acceptors (A) which are interlinked by a $\pi$-conjugated system. The intramolecular charge transfer (ICT) between donor

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Scheme 1. The chemical diagram of (Z)-4-(4-(1-cyano-2-(4-dimethylamino)phenyl)(vinyl)phenyl)-1-methylpyridin-1-ium hexafluorophosphate (a) and (Z)-4-(4-(1-cyano-2-(4-diphenylamino)phenyl)(vinyl)phenyl)-1-methylpyridin-1-ium hexafluorophosphate (b).
and acceptor moieties in D-π-A molecules is well studied.[10] In general, the characteristic of the push-pull properties on the D-π-A chromophore is mainly depending on the electronic behavior of donors and acceptors moieties and also on the length of the π-conjugated linker.[11] The strong electron-donor substituents (N,N-dialkyl or arylamino (–NPh₂) or alkoxy (–OR)) and strong electron-withdrawing moieties (nitro (–NO₂) or cyano (–CN)) are used to construct the D-π-A systems with low band gap and an intense ICT property. Various π-conjugated bridges, including triple or double bonds,[10a, 12] amines,[13] and heteroaromatics,[13d,14] have been used as a π-linker for D-π-A chromophore. Moreover, the band gap and the ICT property of D-π-A molecules can be tuned by changing the donor, acceptor and π-linkers.[15] Ethylene molecules with strong electron-donor and acceptor moieties come also under the category of D-π-A family. The breaking of the C=C bond is rarely observed at the normal condition in the substituted push-pull molecules which contain one donor and one acceptor (HDC=CAH). However, conversion of the zwitterionic form (Scheme 2, b) in the push-pull molecule DD=CAA (Scheme 2, a) with strong D and an acceptor A group has been experimentally confirmed.[16]

Scheme 2. The push-pull ethylene molecule.[16]

The formation of the zwitterionic form (Scheme 2, b) is enhanced by a strong polarization of the molecule due to strong π-electron delocalization between donor and acceptor groups. Because, the electronic perturbation nature of donor and acceptor can enhance the π-electron delocalization on the molecular structure, and it is also reflected on bond lengths as well. The strong π-electron delocalization can significantly be weakened the C=C bond character, and it reduces the electron density around the C=C bond. As a result, the rotation of C=C bond in this class of compounds was observed. The steric factor of substituents (D and A), also plays a crucial role in twisting and elongating the central C=C bond.

Recently, our group has been explored the Z=E transformation of Ia, (Z)-3-[4-(dimethylamino)phenyl]-2-(4-pyridyl)prop-2-enenitrile under different solvent environment, and the Z/E ratio was determined by using 1H-NMR spectroscopy at room temperature.[17] The weakening of the C=C bond character influenced by the solvent effect helps to undergo Z/E transformation. Several studies have explained the structure-property relationship specifically the optical properties of different (Z)-3-substituted phenyl-2-(phenyl/pyridyl)acrylonitrile derivatives (which are belongs to D-π-A system) with different D and A groups.[18]

In this study, we compared the optical and charge transfer properties of the precursors (Scheme 3, (Z)-3-[4-(dimethylamino)phenyl]-2-(4-pyridyl)prop-2-enenitrile (Ia) and (Z)-3-[4-(diphenylamino)phenyl]-2-(4-pyridyl)prop-2-enenitrile (Ib)) with title salts I and II (1-allyl-4-(1-cyano-2-(4-(dimethylamino)phenyl)pyridin-1-ium bromide (I); 1-allyl-4-(1-cyano-2-(4-(diphenylamino)phenyl)pyridin-1-ium bromide (II), (see Scheme 4).

Scheme 3. Chemical diagram for precursor compounds (Z)-3-[4-(dimethylamino)phenyl]-2-(4-pyridyl)prop-2-enenitrile (Ia) and (Z)-3-[4-(diphenylamino)phenyl]-2-(4-pyridyl)prop-2-enenitrile (Ib).

Scheme 4. Chemical diagram of (Z)-1-allyl-4-(1-cyano-2-(4-(dimethylamino)phenyl)pyridin-1-ium bromide (I) and (Z)-1-allyl-4-(1-cyano-2-(4-(diphenylamino)phenyl)pyridin-1-ium bromide (II).

2. Results and Discussion

In this study, we explored the effect of quaternization on the pyridine nitrogen atom in I–II in comparison with their precursor compounds (Ia–IIa), in terms of (i) the push-pull characters, (ii) absorption properties, (iii) the intra- and intermolecular charge transfers (ICT) properties, as well as (iv) intermolecular interactions in the crystalline state. Both salts were obtained from the quaternization reaction of respective precursor compounds (Ia–IIa) with allyl bromide (Scheme 5) by using the synthesis procedures which reported for different alkyaminopyridinium bromide salts.[19] The synthesized salts were characterized by IR, NMR and mass spectrometry.

Scheme 5. Synthesis of salts I–II and Ia–IIa.

Single Crystal X-Ray Crystallography

Both salts (I–II) crystallize in the monoclinic crystal system with space groups P2₁/n for I and P2₁/c for II. Crystallographic data and refinement statistics are presented in Table 1. The ORTEP
Table 1. Crystal data and refinement parameters for I–II.

| Parameters | I   | II  |
|------------|-----|-----|
| Empirical formula | C$_{66}$H$_{148}$N$_{23}$Br$_2$ | C$_{66}$H$_{148}$N$_{23}$Br$_2$ |
| Color, Morphology | dark red, block | red, thick plate |
| Formula weight | 370.29 | 494.42 |
| T(K) | 110 | 110 |
| Wavelength (Å) | 1.54178 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P2$_1$/c | P2$_1$/c |
| a (Å) | 7.45974(14) | 18.8430 (5) |
| b (Å) | 24.9280(4) | 13.1737 (4) |
| c (Å) | 9.6680(19) | 9.7074 (3) |
| α (°) | 90.00 | 90.00 |
| β (°) | 106.020(2) | 95.804 (2) |
| γ (°) | 90.00 | 90.00 |
| V (Å$^3$) | 1728.01(6) | 2397.33 (12) |
| Z | 4 | 4 |
| D$_x$ (g/cm$^3$) | 1.423 | 1.370 |
| μ (mm$^{-1}$) | 3.25 | 1.74 |
| F (000) | 760 | 1016 |
| Crystal size (mm) | 0.21 × 0.17 × 0.15 | 0.40 × 0.27 × 0.08 |
| No. of measured, independent and observed | 11417, 3378, 3266, 5517, | 3001 |
| R1 (I > 2σ(I)) | 0.0271, 0.0317 | 0.0264, 0.0341 |
| wR$_2$ | 0.36 and 0.374 | 0.36 and 0.34 |
| CCDC number | 1863461 | 1863462 |

Figure 1. Displacement ellipsoidal plots (at the 50% probability level) of I–II with atom-numbering scheme.

Figure 2. (a) Overlay of I (green) and Ia (molecule A in form Ia, molecule B in form Ia with atom-numbering scheme. (b) overlay of II and Ila: (c) overlay of I and II (The cation moietiy of I (green) and II (orange) is only used for structural superimposition).

cule in the asymmetric unit. Compound Ila crystallized in the orthorhombic Pbcn space group (refcode: AWECEG0) with one molecule in the asymmetric unit.\(^{[18b]}\) In order to understand the effect of quaternization of the pyridine nitrogen atom in I–II, a detailed structural comparison of I–II and their precursor structures (Ia–IIa),\(^{[18b,c]}\) has been performed. As shown in Figure 2(a), the structure of I is well overlaid with both forms of Ia. Superimposition of I and Ila shows that the quaternized pyridine (ring A) is rotated. In the cases of I and II, the N,N-dimethyl or N,N-diphenyl is slightly rotated and we found that the allyl group exhibits different conformations in these structures (Figure 2(c)). The selected torsion angles clearly show the pyridine ring rotation in II (Figure 2 and Table 2). The bond lengths and torsion angles of I–II and their precursor compounds (Ia–IIa) are summarized in Tables S1–S4, ESI.

To understand the push-pull effect due to the salt formation, I–II, i.e., how the push-pull character is enhanced by the quaternization of pyridine nitrogen when it is compared to their precursor compounds. This comparison is expressed in terms of bond length variation, absorption, charge transfer properties and energy level difference in the frontier molecular orbitals. From Tables S1 and S3, the bond length of C9–C11 in I–II is 1.3723 Å in I which is slightly elongated as compared to the corresponding bond length in II (1.3572 Å). In the precursor, the corresponding bond length is found to be shorter (1.3582 Å in Ia and 1.3482 Å in Ila, see Figures S1–S2). Similar elongation of Csp$^*=Csp^*$ bond length was observed in conjugated ethylene’s molecules in the range of 1.3319–1.3927 Å. Similarly, the bond length of C12–C11 is 1.4293 (Å) in I and 1.4452 (Å) in II being shorter than those of their precursor structures (1.4412 (Å) in Ia and 1.4542 (Å) in Ila). It is to be noted that bond length shortening is also observed for C6–C9 bond length (1.457 (Å) in I and 1.4682 (Å) in II and 1.4812 (Å) in Ia and 1.4872 (Å) in Ila). The shortening and elongation of bonds in the central part of the structures I–II (Figures S1–S2, acrylonitrile group) suggest that the whole molecule participates in the electronic delocalization. The strong conjugation and push-pull characteristc of I–II are mainly due to the stronger electron pulling (−I effect) nature of 4Py$^+$ cation as compared to neutral 4Py cation model found in I–II. This indicates that the electron withdrawing (−I effect) nature of 4Py$^+$ cation in I–II is stronger as compared to the 4Py cation in I–II.

Table 2. The selected torsion angle in I–II and Ia–Ila (°).

| Atoms | Compounds | I | la | II | Ila |
|-------|-----------|---|----|----|-----|
| C5–C6–C9–C11 | −176.02 | −178.41 | 171.92 | −145.62 |
| C7–C6–C9–C10 | −176.52 | −177.51 | 171.52 | −151.62 |
| C9–C11–C12–C13 | −5.74 | −7.02 | −7.53 | 20.53 |
| C9–C11–C12–C17 | 174.12 | 174.01 | 175.52 | −161.32 |
| C14–C15–N3–C18 | 5.63 | 2.42 | 37.62 | 31.92 |
| C14–C15–N3–C19/C24 | −176.82 | −173.81 | −148.42 | −149.61 |
| C16–C15–N3–C18 | −174.62 | −178.21 | −143.02 | −148.61 |
| C16–C15–N3–C19/C24 | 3.13 | 5.62 | 31.12 | 30.02 |
| C1–C2–C3–N1 | 115.52 | −129.62 |
| C2–C3–N1–C4 | 111.02 | −125.32 |
| C2–C3–N1–C8 | −66.12 | 57.12 |

Table 1. Crystal data and refinement parameters for I–II.
The effect of quaternization on the nitrogen atom of pyridine ring in I and II is reflected in the absorption properties when compared to their precursor compounds la and Ila. To understand this, we recorded the absorption spectra for I and II in different solvents (CHCl₃, CH₃OH, ETOH and CH₃CN), and in the solid-state. The absorption maxima (λ_{max}) for I is found at 528 nm in CHCl₃ along with three weak absorption peaks at 315, 291 and 273 nm (Figure 3(a)). For II, λ_{max} is observed at 542 nm and two weak absorptions at 333 and 277 nm in CHCl₃ (Figure 3(b)). The λ_{max} is slightly red-shifted (by 14 nm) in the case of II. In both I and II, the absorption of higher intensity is assigned to S₀→S₁ transition (π→π*), while the weak absorption corresponds to n→π* transition. For comparison, we also acquired the absorption spectra of la and Ila in CHCl₃. The λ_{max} at 422 nm for la and at 427 nm for Ila and these values are very similar with reported values.[8,9]

The results show a strong bathochromic shift in the range of 106–115 nm on the absorption λ_{max} in CHCl₃ for I and II compared to their precursor compounds, la and Ila (Tables 2 and S5). This strong bathochromic shift in I–II is an indication of push-pull effect induced by strong electron withdrawing of 4Py⁺ECN cation. The positively charged 4Py⁺ECN strongly attract the electrons from the electron rich bromide ion (Br⁻) and donor (D). As a result, the push-pull character clearly affects the bond lengths as mentioned above. Moreover, the intermolecular charge transfer (ICT) could arise from the interactions between molecular dipoles and the shifting of electron density of the donor due to the strong pulling of electrons observed earlier.[39]

Furthermore, to understand the solvatochromis properties of salts I–II, we recorded the absorption spectra in CHCl₃, CH₃OH and CH₃CN (Figure 3, (c) and (d)). It can be seen that the absorption peak is nearly the same in protic (CH₃OH) and aprotic (CH₃CN) solvents. Moreover, there is a negative solvatochromis (blue shift; 19–30 nm) observed when increasing the polarity of the solvent. A similar trend is observed in other salts reported earlier.[8,9] The longer λ_{max} of salts I–II in CHCl₃ could be due to the ion-pairs formation in CHCl₃. The similar ion-pairs formation existing in styrylpyridinium iodide in low polar solvents (THF, CHCl₃ and DCM (E° < 0.3)), and its CT absorption characters due to photoinduced electron transfer from iodide to excited singlet state of the cation (styrylpyridinium).[4] In another study, the free ions of stilbazolium salts were found in highly polar solvents (E° < 0.4) and present as ion-pair (contact pairs) in low polar solvents (0.15 < E° < 0.3).[10] Figure 4 shows the solutions of salts I and II in different solvents. The purple color solution (I–II in CHCl₃/DCM) is an indication of strong interactions between cations and anions. The reason for the color change (the orange-red color solution in EtOH/MeOH/ACN) might be due to free ions present in the solution, i.e., less interaction between cation and anion.

### Dipole Moment

To understand the formation of ion pair in solution, the dipole moment (μ) was calculated by DFT method (Table 3). It can be seen from Table 3, in all three solvents, the μ value is higher in the case of salts I and II, whereas the corresponding value is lower for the precursor compounds la and Ila. The dipole
The dipole moment in different solvents could be the reason for color changes.

Absorption Properties in the Solid-state

The solid-state absorption spectra of I–la and II–IIa are shown in Figure 5 (a) and (b), respectively. The solid-state absorption spectra of I–II are very broad compared to la and Ila. A strong bathochromic shift of ∼150 to 200 nm is observed for I and II when compared to la and Ila. This difference is clearly indicating the involvement of allyl moiety in the intermolecular interactions and the presence of interactions between cation and anion in both I and II. Moreover, the interactions are weaker in the solution and thereby weak bathochromic shift (∼50 to 100 nm). The λmax at ∼627 nm for I and 615 nm for II is observed in the solid-state which indicates the presence strong CT between cation and anion in both compounds. It is noted that the very broad absorption peaks in the range of 420–680 nm are observed in I–II, whereas they are not observed in la–IIa which in turn supports for the existence of cation and anion interactions in I–II.

The morphology and color of crystals I–II were recorded using an optical microscope under normal light (Figure 6). The graining powder materials of I–II is in the dark brown color, whereas the single crystals of I–II existing in the metallic bright brown color. The metallic brightness was lost when grinding the crystal to powder. The precursor compounds (la–IIa) exhibit an orange-yellow color and there is no significant color change when crystals were grained to powder.

Theoretical Calculation on Absorption Properties

The electronic transitions of I–II were computed by TD-DFT method in the gas phase, in a solution state (CHCl3, CH3OH and CH3(CN)); and in solid-state (crystal structure geometry), with B3LYP/6-311 + + G (d, p) level of theory. The calculated absorption wavelength (λmax), oscillator strengths (f), and major orbital transitions (in %) for I–II are compared with their respective precursor compounds (la–IIa) (Table 4 and Table S5, ESI). The most important molecular orbitals (HOMO and LUMO) transitions are presented in Figure 7. From Table 4, the computed absorption peaks above 600 nm in both I and II in gas phase correspond to intermolecular charge transfer (ICT) between the 4Py*ECN moiety and bromide ion (Br−) (see Figure 7).

In all three solvents, the computed λmax is blue-shifted as compared to gas and crystal structure geometry (solid-state). It is noted that λmax (above 500 nm in CHCl3 and above 400 nm in MeOH and AcCN solvents) corresponds to ICT between cation and anion. In precursor compounds (la–IIa), the H−1−L is a major transition occurs in gas and in CHCl3 (Table S5). In this transition, there is an intramolecular charge transfer from pyridine ring to other parts of the molecule. Overall, TD-DFT results indicate that the higher absorption in I and II is due to the intermolecular charge transfer between cation and anion.

The energy gap ΔEtot is nearly the same (2.31 eV for I and 2.30 eV for II) and the corresponding value is slightly lower for precursor compounds (la and Ila). However, the energy of HOMO of I and its precursor compound la as well and II and its precursor compound Ila shows a significant amount of energy difference (for I and la:2.59 eV and for II and Ila: 3.12 eV), and similar trend is also observed in the energy of LUMO of I–II and la–IIa (Figure 8). The quaternization on pyridine nitrogen (N1, in salts I–II) makes this energy variation. Based on the above results, we conclude that the contribution of strong electron withdrawing nature of 4Py*ECN moiety made that charge is localized. The strong intra- and intermolecular interactions (between cation and anion) present in the solid-state and in solution state could be the reason for red-shifted absorption in I and II as compared to their respective precursor compounds.

Types of Intermolecular Interactions

The asymmetric units of I–II contain one 1-allyl-4-{1-cyano-2-[4-(dimethyl)diphenylamino)phenyl]vinyl}pyridin-1-ium cation and one bromide anion moiety (Figure 1). In both salts, the cationic molecules are self-assembled by C−H···π, C−H···π interactions whereas the cation and anion moieties are held by C−H···Br− interactions. Various molecular dimers in I–II, which are extracted from the respective crystal structure by using PIXEL method and interaction energies (Eint) for these dimers are listed in Table 5. The interaction energy which is decom-

Figure 5. Absorbance spectra of I and la in the solid-state (a). Absorbance spectra of II and IIa in the solid-state (b).

Figure 6. Single crystals of I–II and powder materials of I–II and la–IIa.
posed into Coulombic ($E_{\text{coul}}$), polarization ($E_{\text{pol}}$), dispersion ($E_{\text{disp}}$) and repulsion ($E_{\text{rep}}$) contributions summarized in Table 5. In I and II, we observed three types of interactions, (i) cation–cation, (ii) cation–anion and (iii) anion–anion interaction only in the case of II. In I, the cationic molecules are self-associated (molecular pairs D6–D11) with the help of several intermolecular C–H–π interactions (dimers D1–D5 in I, and D1–D6 in II) and the $E_{\text{int}}$ values are in the range between $-77.4$ and $-47.0$ kcal mol$^{-1}$ in I and $-81.6$ and $-48.5$ kcal mol$^{-1}$ in II. In II, the cationic molecules are self-assembled through C–H–π, C–H–N and π–π interactions (dimers D7–D12) with the destabilization interaction energy in the range of 35.2–

Table 4. Experimental and computed $\lambda_{\text{abs}}, \lambda_{\text{exp}}$ (in nm) for I and II.

|   | I  | Gas | eV  | $f$  | Major transition (%) | $\lambda_{\text{exp}}$ | II  | DFT | eV  | $f$  | Major transition (%) | $\lambda_{\text{exp}}$ |
|---|---|-----|-----|------|----------------------|-------------------|-----|-----|-----|------|----------------------|-------------------|
| 685 | 1.809 | 0.001 | H-1–L (96) | 692 | 1.792 | 0.001 | H-1–L (96) |
| 668 | 1.854 | 0.020 | H-2–L (62) | 673 | 1.841 | 0.018 | H-2–L (62) |
| 619 | 2.002 | 0.073 | H–L (35) | 627 | 1.976 | 0.096 | H–L (34) |
| 427 | 2.903 | 0.669 | H–L (36) | 475 | 2.609 | 0.844 | H–L (36) |
| 406 | 3.051 | 0.174 | H–L + 1 (20) | 416 | 2.981 | 0.046 | H–L + 1 (76) |
| CHCl$_3$ | | | | | | | | | | | | |
| 522 | 2.374 | 0.009 | H–L (72) | 528 | 2.270 | 0.211 | H–L (58) |
| 516 | 2.403 | 0.002 | H–L (53) | 543 | 2.284 | 0.251 | H–L (40) |
| 474 | 2.617 | 1.294 | H–L (52) | 315 | 3.520 | 0.265 | H–L (22) |
| 341 | 3.639 | 0.003 | H–L + 1 (46) | 293 | 3.600 | 0.021 | H–L + 1 (27) |
| MeOH | | | | | | | | | | | | |
| 441 | 2.891 | 0.005 | H–L (99) | 509 | 2.352 | 1.301 | H–L (97) |
| 424 | 2.921 | 0.003 | H–L (63) | 442 | 2.803 | 0.003 | H–L (71) |
| 425 | 2.920 | 0.006 | H–L (64) | 441 | 2.812 | 0.002 | H–L (27) |
| 337 | 3.676 | 0.014 | H–L + 2 (78) | 352 | 3.514 | 0.246 | H–L + 1 (27) |
| AcCN | | | | | | | | | | | | |
| 474 | 2.615 | 1.345 | H–L (99) | 509 | 2.352 | 1.301 | H–L (99) |
| 429 | 2.891 | 0.005 | H–L (96) | 446 | 2.781 | 0.002 | H–L (97) |
| 424 | 2.921 | 0.003 | H–L (76) | 441 | 2.811 | 0.003 | H–L (69) |
| 423 | 2.932 | 0.005 | H–L (21) | 440 | 2.820 | 0.002 | H–L (27) |
| 337 | 3.678 | 0.014 | H–L + 1 (86) | 352 | 3.513 | 0.245 | H–L + 1 (27) |
| Solid | | | | | | | | | | | | |
| 654 | 1.896 | 0.001 | H–L + 1 (75) | 677 | 1.654 | 0.010 | H–L + 2 (87) |
| 650 | 1.909 | 0.004 | H–L + 1 (76) | 627 | 2.073 | 0.807 | H–L + 3 (89) |
| 602 | 2.059 | 0.065 | H–L + 1 (70) | 525 | 2.363 | 0.008 | H–L + 3 (99) |
| 586 | 2.115 | 0.009 | H–L + 2 (80) | 562 | 2.403 | 0.001 | H–L + 4 (99) |
| 441 | 2.809 | 1.031 | H–L + 2 (78) | 482 | 2.676 | 0.004 | H–L + 5 (99) |

On the other hand, the stabilizing interactions are formed between cation and anion (Br–) moieties with several intermolecular C–H–π–Br– interactions (dimers D1–D5 in I, and D1–D6 in II) and the $E_{\text{int}}$ values are in the range between $-77.4$ and $-47.0$ kcal mol$^{-1}$ in I and $-81.6$ and $-48.5$ kcal mol$^{-1}$ in II. In II, the cationic molecules are self-assembled through C–H–π, C–H–N and π–π interactions (dimers D7–D12) with the destabilization interaction energy in the range of 35.2–
There is a Br···Br interaction occurred with the distance 4.382(1) Å and there is no anion···anion contact in I. Further, the PIXEL interaction energies (∆E_Cp) for different dimers in I and II are compared with the values of ∆E_Cp which is calculated at the crystal geometry of the respective dimer by using the counterpoise method. The E_{tot} and ∆E_Cp values for all dimers are comparable.

Crystal Structure of I

The crystal structure of I can be described as a herringbone pattern (Figure 9). Different molecular pairs identified from the

Figure 7. Electron-density distributions for the frontier molecular orbitals of I–II calculated at the B3LYP/6-311+ + G (d, p) level of theory in the gas phase. The orbitals plotted with isovalue = 0.02 Å⁻³.

Figure 8. The molecular orbital energy levels of I–II and their parent compounds (Ia–IIa; energy in eV). This energy levels are obtained from the optimized geometry in a vacuum with B3LYP/6-311+ + G(d,p) level of theory.

Figure 9. Overall packing arrangement of I in (a) cationic molecules as double arrays and (b) the cation and anion arrangement in I.
The cationic molecules of I in the crystal structure are arranged as arrays which run parallel to crystallographic b axis (Figure 9a). In each array, molecules are interlinked in a head-to-tail (N,N-dimethyl phenyl side)-to-tail (allyl group) manner by an intermolecular C···H–π interaction (D11, $E_{\text{tot}}$: 23.3 kcal mol$^{-1}$). The molecules in one array interact with molecules in the adjacent array through π–π and C–H···π interactions together (D8, $E_{\text{tot}}$: 27.3 kcal mol$^{-1}$). For the π–π interaction, ring B is stacked against the cyano group (C10···N2) and the N,N-

| Motif/ Possible Interactions | Geometry (Å) | Symmetry code | Distance | $E_{\text{tot}}$ | $E_{\text{tot}}$ | $E_{\text{tot}}$ | $E_{\text{tot}}$ | $\Delta E_{\text{tot}}$ | HS label |
|-----------------------------|-------------|---------------|----------|----------------|----------------|----------------|----------------|----------------|----------|
| C21·H21·Br1<sup>−</sup>·Br1<sup>−</sup> | 4.382 | $-x$·$y$, $-z$ | 4.381 | 76.0 | 3.2 | 0.3 | 72.7 | 73.16 |
| C1·H14·C1–C18<sup>−</sup> | 3.621 | 130 | 3.622 | 101 | $1-x$, $3-y$, $1-z$ | 15.298 | 13.5 | 15.0 | 1/2 |
| D10 | 3.621 | 130 | 3.622 | 101 | $1-x$, $3-y$, $1-z$ | 15.298 | 13.5 | 15.0 | 1/2 |
| C14·H14·C1–C18<sup>−</sup> | 3.621 | 130 | 3.622 | 101 | $1-x$, $3-y$, $1-z$ | 15.298 | 13.5 | 15.0 | 1/2 |
| C11·H11·Br1<sup>−</sup> | 2.73 | 3.771 | 162 | x, $1-y$, z | 4.492 | $-71.0$, $-15.6$, $-5.5$ | 10.5 | $-81.6$, $-79.58$ |
| D7 | 2.73 | 3.771 | 162 | x, $1-y$, z | 4.492 | $-71.0$, $-15.6$, $-5.5$ | 10.5 | $-81.6$, $-79.58$ |
| C7–H7·Br1<sup>−</sup> | 2.72 | 3.779 | 167 | x, $1-y$, z | 4.692 | $-41.2$, $-3.4$, $-3.7$ | 0.8 | 35.0 | 36.65 |
| C11–H11·Br1<sup>−</sup> | 2.75 | 3.753 | 154 | x, $1-y$, z | 4.692 | $-41.2$, $-3.4$, $-3.7$ | 0.8 | 35.0 | 36.65 |
| C6·H6·Br1<sup>−</sup> | 2.73 | 3.740 | 133 | x, $3-y$, $1-z$ | 6.158 | $-41.0$, $-8.0$, $2.9$ | 48.5 | $-47.72$ |
| C26·H26·Br1<sup>−</sup> | 2.92 | 3.740 | 133 | x, $3-y$, $1-z$ | 6.158 | $-41.0$, $-8.0$, $2.9$ | 48.5 | $-47.72$ |
| C9·H9·N1<sup>−</sup> | 3.349 | x, $3-y$, $2+z$ | 8.881 | 44.2 | $-5.0$, $-8.1$ | 4.0 | 35.2 | 36.44 |
| C8–C5·N1<sup>−</sup> | 3.503 | x, $3-y$, $2+z$ | 8.881 | 44.2 | $-5.0$, $-8.1$ | 4.0 | 35.2 | 36.44 |
| C2·H2·C7<sup>−</sup> | 3.09 | 3.859 | 129 | x, $3-y$, $2+z$ | 11.935 | 41.9 | $-5.2$, $-6.4$ | 3.0 | 33.2 | 35.76 |
| C23·H23·C23 | 2.35 | 3.542 | 121 | $-x$, $1-y$, $1-z$ | 9.274 | $-65.6$, $-9.7$, $-3.0$ | $-4.0$, $-74.3$, $-73.99$ | $-4.0$, $-74.3$, $-73.99$ |
| C23·H23·H23·C23 | 2.34 | 3.542 | 121 | $-x$, $1-y$, $1-z$ | 9.274 | $-65.6$, $-9.7$, $-3.0$ | $-4.0$, $-74.3$, $-73.99$ | $-4.0$, $-74.3$, $-73.99$ |
| C14·H14·C26<sup>−</sup> | 3.566 | 157 | x, $2-y$, $1-z$ | 7.514 | 22.3 | $-3.7$, $-16.7$, $12.7$ | 14.8 | 19.96 |
| C17·H17·H25·C25 | 2.29 | 3.566 | 157 | x, $2-y$, $1-z$ | 7.514 | 22.3 | $-3.7$, $-16.7$, $12.7$ | 14.8 | 19.96 |
| C29·H29·C20<sup>−</sup> | 2.73 | 3.616 | 139 | x, $2-y$, $1-z$ | 7.514 | 22.3 | $-3.7$, $-16.7$, $12.7$ | 14.8 | 19.96 |
| C20·H20·C23<sup>−</sup> | 2.83 | 3.478 | 119 | x, $2-y$, $1-z$ | 7.514 | 22.3 | $-3.7$, $-16.7$, $12.7$ | 14.8 | 19.96 |
| C21·H21·N2 | 2.61 | 3.525 | 130 | x, $-1/2+y$, $3/2-z$ | 12.524 | 17.5 | $-0.8$, $-3.9$ | 1.6 | 14.5 | 16.23 |
| C28·H28·C19<sup>−</sup> | 2.60 | 3.626 | 101 | $1-x$, $3-y$, $1-z$ | 15.298 | 13.5 | $-2.4$, $-9.9$ | 10.1 | 11.4 | 14.47 |
| C28·H28·H29·C29 | 2.37 | 3.626 | 101 | $1-x$, $3-y$, $1-z$ | 15.298 | 13.5 | $-2.4$, $-9.9$ | 10.1 | 11.4 | 14.47 |

The cationic molecules of I in the crystal structure are arranged as arrays which run parallel to crystallographic b axis (Figure 9a). In each array, molecules are interlinked in a head-to-tail (N,N-dimethyl phenyl side)-to-tail (allyl group) manner by an intermolecular C···H–π interaction (D11, $E_{\text{tot}}$: 23.3 kcal mol$^{-1}$). The molecules in one array interact with molecules in the adjacent array through π–π and C–H···π interactions together (D8, $E_{\text{tot}}$: 27.3 kcal mol$^{-1}$). For the π–π interaction, ring B is stacked against the cyano group (C10···N2) and the N,N-

Crystal structure of I are depicted in Figure S3 along with their intermolecular interaction energies calculated from the PIXEL method.

The cationic molecules of I in the crystal structure are arranged as arrays which run parallel to crystallographic b axis (Figure 9a). In each array, molecules are interlinked in a head-to-tail (N,N-dimethyl phenyl side)-to-tail (allyl group) manner by an intermolecular C···H–π interaction (D11, $E_{\text{tot}}$: 23.3 kcal mol$^{-1}$). The molecules in one array interact with molecules in the adjacent array through π–π and C–H···π interactions together (D8, $E_{\text{tot}}$: 27.3 kcal mol$^{-1}$). For the π–π interaction, ring B is stacked against the cyano group (C10···N2) and the N,N-

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dimethyl group acts as a donor and ring A as an acceptor for the C–H–π interaction. The motif D8 makes the molecules formed as double arrays. The adjacent double arrays are further interconnected by C–H–π interaction (D9, Etot: 27.2 kcal mol⁻¹, Figure 9(a)) to form the herringbone architecture generated by cationic molecules of I. The bromide anions are in the vicinity of allyl group and the anions are placed inside the double arrays in the crystal. Except for ring B, other functional units (allyl, pyridine, acrylonitrile and N, N-dimethyl) are involved in the intermolecular C–H–Br⁻ interactions. A detailed discussion on the arrangement of ion pairs is given in the separate section. Further, the allyl group is involved in the intermolecular C–H–π interactions (C3–H3B–πa in D6; Eπa: 35.0 kcal mol⁻¹ and C14–H14–πa in D11; Eπa: 23.3 kcal mol⁻¹) and the latter interaction plays an important to like the molecules as arrays as mentioned earlier. Furthermore, the cyano group is involved in three-centered intermolecular C–H–N interactions as an acceptor. These interactions (D7, Eπ: 28.1 kcal mol⁻¹) link the neighbouring molecules into a chain which runs parallel to c axis (Figure 10).

Figure 10. Part of the crystal packing of I showing the C16–H16–N2 and C19–H19 A–N2 interactions which link the molecules into a chain.

Crystal Structure of II

The crystal structure of II is presented in Figure 11. Various molecular pairs identified from the crystal structure of II are illustrated in Figure S4, along with their intermolecular interaction energies calculated from the PiXEL method. The crystal structure of II is completely different from that of the crystal structure of I. All the functional units (allyl, pyridine, acrylonitrile, N, N-diphenyl and phenyl) of II participate in the intermolecular C–H–π interactions.

The overall structure can be described as a compact double helical structure in which quarterized pyridine ring placed outside the helical backbone. Both helical chains are formed by intermolecular C–H–π interaction (D10, Eπ: 14.8 kcal mol⁻¹). One of the N, N-diphenyl rings in one helical chain is in a displaced stacking with another N, N-diphenyl ring comes from the neighbouring helical chain at the center. This arrangement is stabilized by C–H–π (D12, Eπ: 11.4 kcal mol⁻¹). The anions are located within the displaced stacking of N,N-diphenyl rings and N, N-diphenyl rings are also located on the helical grooves. The C–H–N interactions in D11 (Eπ: 14.5 kcal mol⁻¹) link the neighbouring molecules into a zigzag chain which runs parallel to b axis (Figure S5). Further, the allyl group has also participated in the intermolecular C–H–π interactions with ring B and acrylonitrile moiety of the cationic molecule (D8, Eπ: 33.2 kcal mol⁻¹) and it also involved in stabilizing interaction (C–H–Br⁻) with anions (D5 with Eπ: –48.6 kcal mol⁻¹). In addition, the substituted N, N-diphenyl groups are engaged in several C–H–π interactions (D9, D10 and D12) and an intermolecular C–H–Br⁻ interaction (D6, Eπ: –48.5 kcal mol⁻¹). It is noted that the atom C4 of the pyridine ring interacts with an anion (C–Br⁻ interaction; motif D3; Eπ: –74.3 kcal mol⁻¹) and its existence was confirmed by the QTAIM analysis. The Eπ value for C4–Br⁻ contact is 1.10 kcal mol⁻¹.

To confirm the existence of various noncovalent interactions observed in different molecular pairs, the topological properties were computed for the intermolecular interactions at the bond critical points in I and II (Table S6, ESI) and molecular graphs for these dimers are illustrated in (Figures, S6 and S7, ESI). The stabilizing energies (Eπ) calculated by QTAIM approach for these interactions are in the range of 0.94 (motif D4) –
2.31 (motif D1) kcal mol\(^{-1}\) in I and 0.98 (motif D5) – 3.88 (motif D2) kcal mol\(^{-1}\) in II. The corresponding values are found to be in the range of 0.5 (D6) – 1.54 (D11) kcal mol\(^{-1}\) for C–H–π interactions in I (0.5 (D7) – 1.89 (D10) kcal mol\(^{-1}\) in II). The \(E_{\text{HB}}\) value for the C–H–N is calculated to be 0.98 (D7 in I) kcal mol\(^{-1}\) and 1.28 (D11 in II) kcal mol\(^{-1}\). This result suggests that some of the C–H–π and C–H–N interactions energies are slightly stronger in II. In addition, there are four H–H interactions observed in different molecular pairs \((E_{\text{HB}}\text{ of 0.8 kcal mol}^{-1}\) in D9 and 1.2 kcal mol\(^{-1}\) in D12) and these interactions provide additional stabilization to the crystal structure along with other types of interactions in II. It should be noted that there is no H–H type of interaction observed in I.

To understand the relationship between the topological parameters (particularly, electron density (\(\rho\)) and the Laplacian electron density (\(\nabla^2 \rho\)) and bond path distance \((R_b)\) at the BCP’s between the interacting atoms. It is noted that the H–Br interactions in I and II display the trend of exponential decay (with \(R^\alpha > 0.98\)) in the magnitude of electron density (\(\rho\)) and the Laplacian electron density (\(\nabla^2 \rho\)) with the increasing length of bond path (Figure S8, ESI).

### Arrangement of Ion Pairs in the Crystal Structures of I and II

Figure 12 describes the arrangement of ions (the centroid is taken for cationic molecule) in the crystal structures of both salts. The bromide ions in I arranged as double ions in a zigzag manner which runs parallel to the a axis and the inter-ionic distance within double ions is 6.096 Å and the adjacent double ions are separated by 7.554 Å. Similarly, the cationic molecules are also arranged as double cations with the inter-ionic distance being 4.655 Å and the adjacent double ions are placed at a distance of 5.125 Å. Overall, alternate cationic and anionic zigzag chains are arranged in the crystal structure. However, the arrangement of cations and anions are completely different in II as compared to the crystal structure of I. The anions are formed as double arrays and these arrays are sandwiched between the cationic arrays. The distance between two anionic arrays is \(-84.2\) kcal mol\(^{-1}\) than I \(-16.9\) kcal mol\(^{-1}\). The larger difference on the lattice energy between I and II is might be due to the presence of N, N-diphenyl group in II which helps to pack the molecules more compact. The lattice energy difference is in good agreement with the melting points of I and II \((\sim 20^\circ\text{C} \text{ higher in II})\). In the case of II, a notable increase of Coulombic and polarization energies (the contribution of Coulombic energy is 3 fold higher and polarization energy is approximately 2 fold higher as compared to I) is observed. The contribution of repulsive energies is also more pronounced in II than other structures due to compact crystal packing.

### NBO Analysis

In order to learn the origin of intermolecular charge transfer process between cation and anion moieties in I and II, we performed NBO analysis for various dimeric pairs formed by intermolecular C–H–Br interactions. The second order perturbation energies for different donor-acceptor NBOs are summarized in Table 7. The results suggest that the interactions between the lone pair orbitals of the anion and the CH groups (anti-bonding) of the pyridine ring are observed to give the strongest stabilization energy in both I and II. We note that the charge transfer \([\text{LP}(4) \text{ Br}–\text{BD}^*(\text{C8–H8})]\) is even stronger in II. The allyl group is also involved in the intermolecular charge transfer process with the moderate stabilization energy. Moreover, all the CH groups of allyl moiety is participated in the charge transfer in I, while C2–H and C3–H groups in II are not involved in the charge transfer because the allyl group adopts different conformation as compared to I. The interaction between anti-bonding orbital of C11–H11 group and LP(4) Br anion is more stronger (3.92 kcal mol\(^{-1}\)) in II. The corresponding interaction is slightly weaker (1.58 kcal mol\(^{-1}\)) in I.

![Figure 12](image-url)
Hirshfeld Surface Analysis

It is well known that the HS analysis is a useful visualization tool for the analysis of intermolecular interactions in the crystal packing and FP analysis is also used to quantify the contribution of various intermolecular contacts present in the crystal structures. The HS mapped with $d_{norm}$ was obtained for I–II and their precursor molecules (Figure 13). The close contacts observed in these structures are labelled (see Table 5). Nine intermolecular interactions (label 1–9) are visible on the HS of I whereas there are 10 intermolecular close contacts (label 10–19) seen on the HS of II.

A close examination of the FP generated for I–II and their precursor molecules indicating that the intermolecular H···H interactions are predominant (Figure 14 and 15). In II, the intermolecular C···H/C contacts are contributing 30.1% to the total HS area. This contact is reduced to 20.2% in I and this reduction is compensated by intermolecular C···C, N···H and H···Br interactions contacts. This is clearly supporting the presence of more C···H/C interactions in II and presence of π···π interactions in I. It should be emphasized that the H···N is decreased in II when compared to its precursor molecule (AWEGEQ) and other contacts are comparable. It is to be noted that the relative contribution of all types of contacts observed in I is altered as compared to its precursor (different forms) molecule.

3. Conclusions

The variation in the optical properties due to the formation of the respective quaternary salts and due to the charge transfer (CT). It was also due to the strong effect on the structure of the electron acceptor group of the quarternized salts. In the solid-state absorption spectra, there was a broadening of the peak in the salts and this broadening was absent in precursor compounds. This observation had clearly highlighted the effect of quarternization. Further, the variation of bond lengths of selected bonds observed in the crystal structures was supported for the existence of a strong push-pull character of I–II. Due to the strong push-pull nature of I and II, there was a red-shift (<100 nm) observed in the absorption because of the presence of 4Py*ECN moiety. The charge transfer occurred between cation and anion was confirmed through DFT calculation. The arrangement of cations and anions are completely different in the crystal structures of I (herringbone) and II (double helical).

Table 7. Selected cation-anion charge transfer process in I–II and its corresponding second order perturbation energy ($E^{(2)}$ in kcal mol$^{-1}$).

| Dimer | Compound I | Aceptor NBO | $E^{(2)}$ | Compound II | Aceptor NBO | $E^{(2)}$ |
|-------|------------|-------------|----------|-------------|-------------|----------|
| D1    | LP (4) Br  | BD*(1) C7–H7| 5.64     | LP (4) Br  | BD*(1) C7–H7| 4.15     |
|       | LP (4) Br  | BD*(1) C11–H11| 1.58    | LP (4) Br  | BD*(1) C11–H11| 3.92    |
| D2    | LP (4) Br  | BD*(1) C3–H3B| 3.34     | LP (4) Br  | BD*(1) C8–H8| 10.53    |
| D3    | LP (3) Br  | BD*(1) C1–H1A| 1.31     | LP (4) Br  | BD*(1) C1–H1B| 0.43    |
| D4    | LP (4) Br  | BD*(1) C4–H4| 6.19     | LP (4) Br  | BD*(2) C4–H4| 3.57     |
| D5    | LP (4) Br  | BD*(1) C19–H19B| 4.18   | LP (3) Br  | BD*(1) C1–H1B| 1.22    |
| D6    | LP (4) Br  | BD*(1) C3–H3A| 0.57     | LP (3) Br  | BD*(1) C1–H1B| 0.73    |

Figure 13. Views of the Hirshfeld surface mapped with $d_{norm}$ in two different orientations for I and II with their precursor compounds (Ia for TENMIK-A, TENMIK-B and TENMIK01; Ila for AWEGEQ). The significant contacts are labelled. To refer Table 5 for the more details about the interactions.
As shown in Scheme 5, the compound (Z)-3-(4-(dimethylamino)phenyl)-2-(pyridin-4-yl)-acrylonitrile (Ia) and (Z)-3-(4-(diphenylamino)phenyl)-2-(pyridin-4-yl)-acrylonitrile (Ia) were synthesized from 4-N,N-substituted aminobenzaldehyde ( Ib–Iib) and 4-(cyanomethyl)pyridin-1-ium chloride (Z) as reported earlier. The mixture of Ia or Ila (1 mmol) and allyl bromide (3, 1.1 mmol) in 25 mL of acetonitrile were refluxed for 12 h. Upon completion of the reaction, the reaction mixture was cooled down to room temperature and the salts (I–II) were settled as precipitates. The precipitates were collected by vacuum filtration and washed with acetone. The products (I–II) were dried under vacuum. Both salts (I–II) were purified by recrystallization from acetonitrile and methanol (1:1 v/v) mixture.

**Synthesis of (Z)-1-allyl-4-(1-cyano-2-(4-(dimethylamino)phenyl)-vinyl)pyridin-1-ium Bromide (I)**

The reaction was carried out as mentioned in the general procedure using (Z)-3-(4-(dimethylamino)phenyl)-2-(pyridin-4-yl)-acrylonitrile (Ia, 250 mg, 1 mmol) and allyl bromide (3, 135 mg, 1.1 mmol), conditions: refluxed for 12 h. The compound I was obtained as purple colour solid (300 mg, 80% yield). The compound I was purified by the recrystallization from methanol and acetone (1:1 v/v) mixture. m.p 198–200°C. IR (KBr) 3005, 2675, 2597, 2208, 1638, 1610, 1556, 1521, 1450, 1370, 1231, 1198, 1160, 850, 531 cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): δ 8.90 (d, J = 7 Hz, 2H), 8.54 (s, 1H), 8.27 (d, J = 7 Hz, 2H), 8.09 (d, J = 9 Hz, 2H), 6.93 (d, J = 9.5 Hz, 1H), 6.21–6.13 (m, 1H), 5.5–5.38 (m, 2H), 3.25 (s, 6H); ¹C NMR (125 MHz, DMSO-d₆): δ 134.0, 121.6, 67.1, 65.9, 100.2, 112.6, 116.8, 123.0, 124, 130.3, 130.7, 150.0, 155.5, 158.4, 170.7, 172.5. Mass (Direct, EI⁻ method): 290 (M⁻), 265, 249(100%), 221.

**Synthesis of (Z)-1-allyl-4-(1-cyano-2-(4-(diphenylamino)phenyl)-vinyl)pyridin-1-ium Bromide (II)**

The reaction was carried out as mentioned in the general procedure using (Z)-3-(4-(diphenylamino)phenyl)-2-(pyridin-4-yl)-acrylonitrile (Ia, 100 mg, 0.26 mmol) and allyl bromide (3, 35 mg, 0.29 mmol), conditions: refluxed for 12 h. The compound II was obtained as deep brown colour solid (105 mg, 82% yield). The product was purified by the recrystallization from methanol and acetone (1:1 v/v) mixture. m.p 219–220°C. IR (KBr) 3174, 3089, 3057, 2963, 2927, 2781, 2598, 2204, 1588, 1486, 1410, 1375, 1302, 1249, 1230, 1198, 1160, 800, 740, 680, 603, 531 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 9.09 (d, J = 10 Hz), 8.54 (s, 1H), 8.40 (d, 2H, J = 10 Hz), 8.13 (d, 2H, J = 10 Hz), 7.41–7.37 (m, 4H), 7.26–7.24 (m, 2H), 7.22–7.21 (m, 4H), 6.97 (d, 2H, J = 10 Hz), 6.17–6.09 (m, 1H), 5.64–5.54 (m, 4H); ¹C NMR (125 MHz, CDCl₃) δ 153.4, 152.1, 151.6, 145.1, 143.9, 134.5, 130.0, 129.9, 126.8, 126.1, 124.1, 123.9, 122.5, 118.6, 117.1, 98.0, 62.5. Mass (Direct, EI⁻ method): 414 (M⁻), 373 (100%), 345, 294, 268, 241.

**Experimental Section**

**Synthesis and Crystallization**

**General Experimental Procedure for the Synthesis of Salts I–II**

As shown in Scheme 5, the compound (Z)-3-(4-(dimethylamino)phenyl)-2-(pyridin-4-yl)-acrylonitrile (Ia) and (Z)-3-(4-(diphenylamino)phenyl)-2-(pyridin-4-yl)-acrylonitrile (Ia) were synthesized from 4-N,N-substituted aminobenzaldehyde (Ib–Iib) and 4-(cyanomethyl)pyridin-1-ium chloride(Z) as reported earlier. The mixture of Ia or Ila (1 mmol) and allyl bromide (3, 1.1 mmol) in 25 mL of acetonitrile were refluxed for 12 h. Upon completion of the reaction, the...
Single Crystal X-Ray Diffraction (SCXRD)

The intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu Kα radiation (λ = 1.54178 Å) for I and Mo Kα radiation (λ = 0.71073 Å) for II. The program CrysAlisPro (Versions 1.171.36.32 Agilent Technologies, 2013 or 1.171.39.29c, Rigaku OD, 2017) was used to refine the cell dimensions and for data reduction. The structures were solved with the program SHELXS-97[25] and were refined on F² with SHELXL-2014/2.[26] An analytical numeric absorption correction using a multifaceted crystal model or a numerical absorption correction based on Gaussian integration over a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AXIF 23, AXIF 43, AXIF 93 or AXIF 137 with isotropic displacement parameters having values 1.2 or 1.5 Ûeq of the attached C atoms. The crystal data refinement parameters are summarized in Table 1. Displacement ellipsoid plots and crystal packing figures were made using the programs PLATON[24] and MERCURY,[21] respectively.

Hirshfeld Surface Analysis, and PIXEL Energy Calculation

The Hirshfeld surfaces (HS) analysis[24–ca. 24] and the decomposed two-dimensional fingerprint plots (FP)[27] was used to quantify the contribution of different intermolecular interactions existing in the crystal structure and to understand the nature of intermolecular interactions. The HS and FP were generated using the program CrystalExplorer17.[28] Further, the intermolecular interaction energies (Eint) for different molecular pairs of I–II were calculated using the PIXEL method (in the CLP computer program package version 12.5.2014).[29] Based on the Eint values, the selected molecular pairs were considered for further analysis. The total lattice energies of the title salts(I–II) and their precursor compounds (Ia–IIa) were also computed using the PIXEL method. The C–H bond lengths were adjusted to typical neutron diffraction values (C–H = 1.089 Å) before the HS and PIXEL calculations. For PIXEL calculations, the electron density of the molecules was obtained at MP2/6-31G** level of theory using Gaussian09 for all the molecules in the current study.

Quantum Chemical Calculations

All the quantum chemical calculations were performed with the Gaussian 09 program package.[30] For structural optimization, the respective crystal structure geometry was used for I–II and Ia–IIa as a starting model. These structures were fully optimized using M05-2X[31]/cc-pVTZ level of theory with the incorporation of Grimme’s D3 dispersion corrections.[32] The selection of M05-2X functional and basis set has been made based on our earlier studies.[33] The vibrational frequency was calculated for the optimized structures in the gas phase in order to ascertain the global minima on the potential energy surface and was found to have no negative frequencies. Further, the interaction energies (ΔEint) for the various molecular dimers at their crystal geometry were calculated at M05-2X/cc-pVTZ level of theory. The ΔEint was corrected for basis set superposition error (BSSE)[34] using the counterpoise method. To explore the solvent (chloroform, methanol and acetonitrile) influence, we used the conductor-like polarizable continuum model (CPCM)[35] for all solution-phase structural optimization. Time-dependent DFT (TD-DFT)[36] approach was used to calculate the absorption properties with B3LYP/6-311 + + G(d, p) level of theory. Furthermore, we performed natural bond orbital (NBO) analysis to characterize the nature of charge transfer between the cation and anion moieties in I and II.

Analysis of Topological Parameters (QTAIM Calculations)

We performed topological analysis on the selected dimers by using the AIMALL package (T. A. Keith, AIMALL, version 16.05.18; TK Gristmill Software, Overland Park KS, USA, 2013). For this purpose, the DFT calculation (with the density= current keyword) for the selected molecular pairs at their crystal geometry was performed at the MP2/6-31G** level of theory. The dissociation energies for different intermolecular interactions at the bond critical point (BCP) were estimated using two empirical approaches as proposed earlier,[37] (i) D.E.(int) = −0.5Vb (a.u.)[37] (ii) D.E.(int) = 0.429Gb, (a.u.) Where D.E.(int) is the dissociation energy of the interaction (interaction energy (Eint) = −D.E.(int)),[37] Vb and Gb are the local potential and kinetic energy density at the bond critical points (BCP’s), respectively.

UV-Vis Absorbance

The absorbance spectra were measured using a spectrometer SD2000 (Ocean Optics, Dunedin, FL) with a DT 1000 CE light source (Analytical Instrument Systems, Inc, Flemington, NJ). For powder samples, the absorption spectra were measured using the Spectrometer Cary 300 (Agilent) in the mode the diffuse reflectance.

Supporting Information

Supporting information for this article is given via a link at the end of the document.(bond length and torsion angle comparison of I–II and their precursor structures (Ia–IIa); Experimental and computed V_âh (in nm) for Ia and IIa; Different interacting dimers in the crystal structure of I and II along with the interaction energies in kcal mol⁻¹ and selected topology parameters and molecular graph with BCP’s for an individual dimers in I and II.)

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Conflict of Interest

The authors declare that there is no conflict of interest.

Keywords: bromide salts · quaternary salts · optical properties · intermolecular interactions · DFT calculation
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