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Structural Characterization of Quaterphenyl Cation Radical: X-ray Crystallographic Evidence of Quinoidal Charge Delocalization in Poly-*p*-phenylene Cation Radicals

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The study of π-conjugated oligomers and polymers has attracted considerable attention since these materials hold promise for applications in the emerging area of molecular electronics and nanotechnology.[1] Of these, poly-*p*-phenylenes (PPP) are especially important due to their optoelectronic properties,[2] high conductivity when doped with either n- or p-type dopants,[3] potential usage as active constituents of blue light emitting diodes,[4] and high thermal and oxidative stability.[5] Unfortunately, their lack of processability, especially when they are unsubstituted, has hampered their study as well as exploitation of their extensive potential for practical applications.[6]

Several studies have been conducted where PPP oligomers have been utilized as spacers or bridges in molecular assemblies consisting of electron donor−bridge−electron acceptor (D−B−A) to explore their potential as functional molecular wires for long-range electron transport.[7] The mechanism of charge transport (CT) in these assemblies is proposed to occur by a combination of highly distance-dependent coherent (i.e., superexchange) and weakly distance-dependent noncoherent (i.e., hopping) mechanisms.[7] In order to gain a better understanding of various CT mechanisms operating in these PPP-based molecular wires, a quantitative understanding as to how the charge is stabilized by multiple aryl moieties that constitute the spacer is highly desirable. Therefore, attempts to isolate an oxidized polyphenyl cation radical to gain X-ray crystallographic evidence as to how the creation of a hole leads to structural changes in various PPPs are pertinent. We have recently undertaken studies to this effect, and herein we report the isolation of both the neutral as well as the cation radical salt of a quaterphenyl derivative (QP) having *tert*-butyl solubilizing groups at the terminal positions, enabling us to unequivocally establish from the crystallographic parameters that a single charge is delocalized by a quinoidal distortion of the phenylene rings. It is also noted that the *tert*-butyl substitutions at terminal positions in larger PPP oligomers merely aid in improving their solubility without affecting the electronic properties to any significant extent as the HOMO resides largely on the central phenylene rings.[8] The details of these preliminary finding are discussed herein.

The 4,4′′′′-di-*tert*-butylquaterphenyl was prepared from 4,4′′-diiodobiphenyl and 4-*tert*-butylphenylboronic acid via a Pd(0)-mediated Suzuki reaction in 67% yield and was purified by crystallizations from a $CHCl_3$−MeOH mixture (see Supporting Information for the experimental details and spectral data).

Next, the quaterphenyl derivative was subjected to electrochemical oxidation at a platinum electrode as a 2×10^{-3} M solution in dichloromethane containing 0.2 M *n*-Bu_4NPF_6 as the supporting electrolyte. The cyclic voltammograms (Figure 1A) consistently met the reversibility criteria at various scan rates of 25−400 mV/s, as they all showed cathodic/anodic peak current ratios of $i_a/i_c = 1.0$ (theoretical) as well as the differences between anodic and cathodic peak potentials of $E_{pa} - E_{pc} \sim 70$ mV at 22 °C. The reversible oxidation potential was calibrated with ferrocene as internal standard ($E_{ox} = 0.45$ V vs SCE) and was found to be 1.47 V versus SCE corresponding to the formation of a monocation.

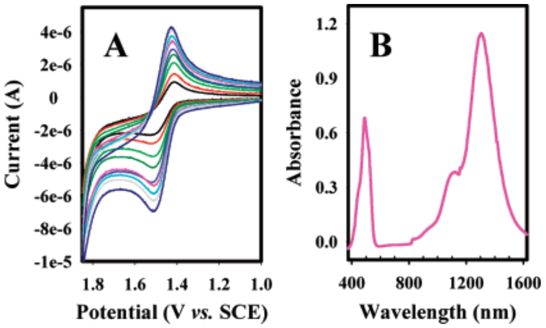

Figure 1. (A) Cyclic voltammograms of 2×10^{-3} M QP in CH_2Cl_2 containing 0.1 M *n*-Bu_4NPF_6 at scan rates between 25 and 400 mV s^{-1}, and (B) UV−vis absorption spectrum of cation radical $QP^{+\bullet}$ obtained by $NO^+SbCl_6^-$ oxidation in dichloromethane at 22 °C.

The high electrochemical reversibility of oxidation of QP prompted us to isolate its cation radical in solution by chemical oxidation using nitrosonium hexachloroantimonate as a 1-e$^-$ oxidant according to the stoichiometry in eq 1.

$$\mathrm{QP} + \mathrm{NO}^+\mathrm{SbCl}_6^- \xrightarrow[-10\ ^\circ\mathrm{C}]{\mathrm{DCM}} \mathrm{QP}^{+\bullet}\mathrm{SbCl}_6^- + \mathrm{NO}\uparrow \qquad (1)$$

Thus, a solution of QP in anhydrous dichloromethane was added to crystalline $NO^+SbCl_6^-$ under an argon atmosphere at −10 °C. The gaseous nitric oxide produced was entrained by bubbling argon through the solution to yield a deep red solution, which upon spectrophotometric analysis indicated the formation of $QP^{+\bullet}SbCl_6^-$ as judged by the appearance of characteristic twin absorption bands at $\lambda_{max} = 490$ and 1302 nm (Figure 1B).[9] Twin absorption bands in $QP^{+\bullet}$ are reminiscent of the absorption bands observed in the spectrum of the biphenyl cation radical generated by laser flash photolysis or pulse radiolysis.[10] The molar extinction coefficient of pink-red $QP^{+\bullet}$ was estimated to be $54\,800 \pm 3000$ M^{-1} cm^{-1} (see Supporting Information).

The stability of the $QP^{+\bullet}SbCl_6^-$ prompted us to attempt the isolation of its crystalline salt as follows. For example, an excellent crop of dark red crystals, suitable for X-ray crystallographic studies, were obtained by a slow diffusion of toluene in a dichloromethane solution of $QP^{+\bullet}SbCl_6^-$ during a period of 2 days at −30 °C.

The crystal structure of the $QP^{+\bullet}SbCl_6^-$ revealed that two symmetrically independent molecules of $QP^{+\bullet}$ having essentially the same structure are stacked as dimeric pairs which are separated by intercalated toluene molecules, as shown in Figure 2. The close interplanar distance between the two $QP^{+\bullet}$ in the dimeric pair of ~3.1 Å, which is less than the equilibrium van der Waals separation of 3.4 Å, is indicative of electronic coupling between them.[11] Such

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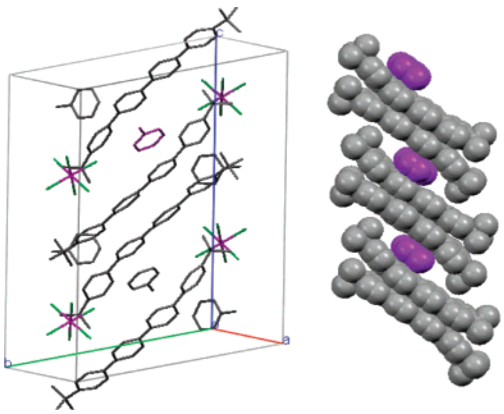
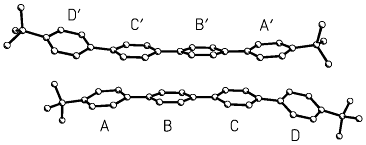


Figure 2. The crystal structure of QP$^{+\bullet}$SbCl$_6^-$ cation radical, with the packing diagram showing that the toluene molecules are embedded between the stacked dimeric pairs.

a close packing of the QP$^{+\bullet}$ in dimeric pairs leads to a slight longitudinal displacement with respect to each other to compensate for the steric crowding caused by the terminal *tert*-butyl groups.

A closer look at the structural parameters of the cation radical QP$^{+\bullet}$, along with a comparison with its neutral form, points to four important observations:



(i) The central bond distance of 1.440 Å between the two inner benzene rings B and C in QP$^{+\bullet}$ is considerably shorter than the two peripheral C−C bonds between the outer rings and the penultimate ones (i.e., 1.454 Å between rings A and B and 1.463 Å between rings C and D). This represents a contraction of the central C−C bond (between ring B and C) by 5 pm in the oxidized form in comparison to 1.1 pm in neutral QP.[12] (ii) The longitudinal bonds inside the rings are contracted, whereas the transverse bonds are lengthened in comparison to neutral QP, indicative of a quinoidal bond alteration.[13] In numerical terms, the longitudinal bond contraction results in bond lengths of 1.377 Å (ring A), 1.362 Å (ring B), 1.368 Å (ring C), and 1.381 Å (ring D) from an average of 1.38 Å in the neutral QP and a consequent lengthening of the transverse bonds to 1.397/1.409 Å (ring A), 1.419/1.424 Å (ring B), 1.421/1.413 Å (ring C), and 1.407/1.399 Å (ring D). The magnitude of the bond contractions and expansions reaches a maximum in the inner rings with the peripheral rings being less affected. (iii) The torsional angles between the rings A/B/C are ∼0.1−15°, resulting in a nearly coplanar conformation. However, for the peripheral ring D, this angle slightly increases primarily due to the steric hindrance of the *tert*-butyl group of the adjacent stacked molecule. Thus, the formation of the cation radical smooths out the torsional motion of the interconnected aryl rings from their typical values of ∼30° between the outer rings and ∼10° between the central rings as in the neutral form, in order to allow effective stabilization of the cationic charge by quinoidal distortions.[13] (iv) Considering the magnitude of quinoidal distortion to be a linear function of the amount of charge allocated within the corresponding ring, we can estimate that the rings A−D bear the following positive charges: 0.15 e (A), 0.46 e (B), 0.33 e (C), and 0.06 e (D). As such, the asymmetric charge distribution further attests to the strong electronic coupling within the "shifted" dimeric associates.[11]

These salient features of the QP cation radical can only be rationalized, when one considers that the single charge is stabilized by a quinoidal valence bond resonance structure. Such a resonance form having a quinoidal structure leads to unequal bond distortions in the aryl rings as well as planarization of the aryl rings for effective π-conjugation with the magnitude of changes being the highest in the central rings. It is worthwhile to note that a previously reported ab initio SCF-LCAO-MO calculation of a lithium-doped quaterphenyl anion radical showed a similar quinoidal distortion as observed herein for the QP$^{+\bullet}$.[14]

In summary, the isolation and X-ray crystal structure determination of QP$^{+\bullet}$SbCl$_6^-$ provides unequivocal evidence for the quinoidal stabilization of the cationic charge or polaron, which is responsible for the high conductivities in PPP oligomers in their doped state. The defect state induces regions of quinoidal conformation and thus serves as a physical model for the insulator−metal transition in PPP.[3] Studies are underway for a more comprehensive investigation of the optoelectronic properties of PPP oligomers and will be reported in due course.

Acknowledgment. We thank the National Science Foundation (CAREER Award) for financial support.

Supporting Information Available: Preparation and spectral data for QP and the X-ray structural data for the neutral QP, QP$^{+\bullet}$SbCl$_6^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0720356