Adiabatic Electron Affinities of Oligophenyls: Anion Photoelectron Spectroscopy and Density Functional Theory Study

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Adiabatic electron affinities (EA_a's) of seven oligophenyls: biphenyl (BP), 4-cyanobiphenyl (CNBP), *o*-terphenyl (*o*-TP), *m*-terphenyl (*m*-TP), *p*-terphenyl (*p*-TP), *p*-quaterphenyl (*p*-QP), and 1,3,5-triphenylbenzene (TPB), have been evaluated by anion photoelectron spectroscopy and density functional theory calculations. The result provides the direct determination of the EA_a values of the isolated CNBP, *p*-TP, *p*-QP, and TPB molecules, while EA_a of BP, *o*-TP, and *m*-TP were estimated from the extrapolation of EA_a vs cluster size. The excellent agreement between the experimental and calculated EA_a were obtained.

Conjugated oligomers are of immense current interest for application in organic light-emitting diode (OLED) and field-effect transistors (FET).[1] Charge carriers in such organic materials are localized and usually characterized as a molecular anion (electron) and cation (hole). Hence, the adiabatic ionization energy (IP_a) and electron affinity (EA_a) of the single (gas-phase) molecule are the leading parameters determining the energy levels of charge transport in organic materials.

So far, rich experimental data concerning IP_a of π-conjugated oligomers have been accumulated by various methods such as ultraviolet photoemission spectroscopy for the gaseous state. In contrast, experimental data pertaining to EA_a of π-conjugated oligomers are still poor at present. For example, oligophenyls have recently attracted interest for application in OLED[2] and FET;[3] nevertheless, no experimental EA_a has been hitherto reported for these compounds.

Accurate determination of EA_a of the isolated molecules can be experimentally performed using gas-phase anion photoelectron spectroscopy. In this letter, we report an anion photoelectron spectroscopy and density functional theory (DFT) study for seven typical oligophenyl compounds: BP, CNBP, *o*-TP, *m*-TP, *p*-TP, *p*-QP, and TPB. The EA_a values of the isolated CNBP, *p*-TP, *p*-QP, and TPB molecules were positive and directly determined experimentally. Because of no bare anion formation, EA_a's of BP, *m*-TP, and *o*-TP were estimated from those of the corresponding dimer anions. The experimental EA_a's thus determined are compared with the calculated counterparts.

The experiments were performed with a magnetic-bottle time-of-flight photoelectron spectrometer. Details of the experiment have been described previously.[4] Briefly, the sample vapor was entrained in helium carrier gas at a stagnation pressure of 5–70 atm and underwent a supersonic expansion. Anion species were produced by high-energy electron impact ionization at the dense part of a free jet. The anions in the beam were coaxially extracted by applying a pulsed electric field (−1.5 kV) and were detected with an in-line TOF-MS having a mass resolution $M/\Delta M \approx 150$. The target anions were selected and decelerated before photodetachment which was initiated by 1.165 eV (1064 nm) photons of fundamental output of Nd:YAG-laser. The energy resolution of the photoelectron apparatus was ca. 50 meV full width at half-maximum (FWHM) for 1 eV electrons. The electron kinetic energy scale was carefully calibrated using the known spectra of Au^-.

Density functional theory calculations of neutral and anionic structures, energies, and harmonic vibrational frequencies of oligophenyls were carried out with Gaussian 98 program.[5] In the current study, the 6-31+G* basis set and B3LYP functional[6] were used for accurate predictions of the electron affinities, because it has been demonstrated that this level of theory well reproduces the experimental EA_a of several aromatic hydrocarbons.[7] Full geometry optimization was performed for each molecule[8] and no imaginary frequency was calculated for any species treated. EA_a was obtained by subtracting the total energy of the optimized anion geometry from the total energy of the optimized neutral geometry.

Figure 1 (left-side) shows the photoelectron spectra of CNBP, *p*-TP, *p*-QP, and TPB taken at 1064 nm. In the spectra of CNBP^- and *p*-TP^-, the lowest-energy peak is most prominently observed with vibrational features and can be straightforwardly assigned to the origin (vibrationless) transition from the anion ground state to the neutral one. In contrast, the lowest-energy peak in the spectra of *p*-QP^- and TPB^- is much weaker than the second peak. If the first peak is due to hot band transitions or minor structural isomers, the intensity of this peak should depend on the source conditions to some extent. However, this peak was always observed and its intensity relative to other peaks was invariant even when stagnation pressure and time interval between the opening of the pulsed valve and the ion acceleration pulse were changed to prompt cooling of molecular anions. Thus, we concluded that the first peak is due to the origin transition from the ground state of the anion to that of the neutral. The EA_a values thus determined are summarized in Table 1.

Meanwhile, the bare anions of BP, *o*-TP, and *m*-TP are absent in the mass spectra, and the continuous formation of their cluster anions begins at the dimer anions. In order to estimate the experimental EA_a values of these molecules, the photoelectron spectra of the dimer anions were measured, and they are presented in Figure 1 (right-side). Unlike the monomer, there are intermolecular coordinates in the dimer, and thus it is difficult to extract "true" EA_a of the dimer from the spectrum. Assuming that there is only a small structural change between the dimer anion and the dimer neutral, we assigned the lowest-energy peak (obtained by the deconvolution with a set of Gaussian functions) as the origin-containing transition. As the result, the EA_a of

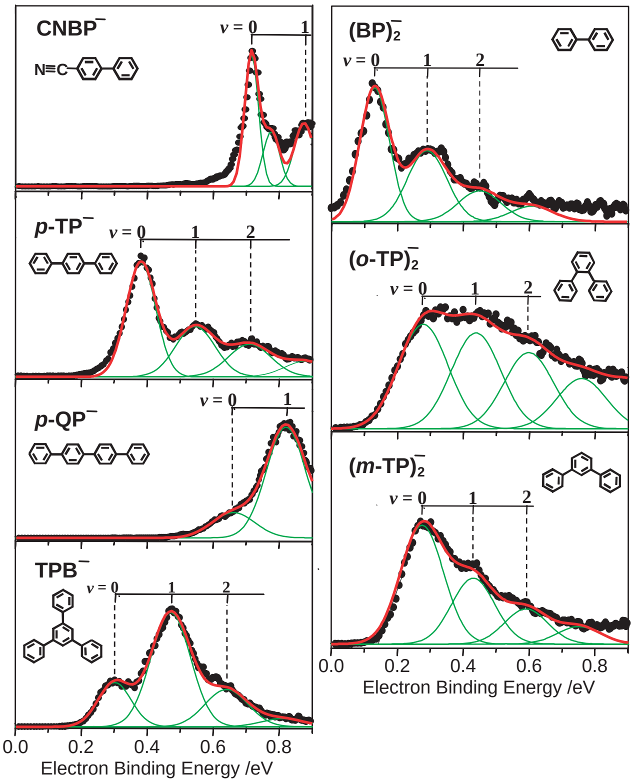

Figure 1. Photoelectron spectra of $CNBP^-$, p-TP^-, p-QP^-, TPB^-, $(BP)_2{}^-$, $(m\text{-}TP)_2{}^-$, and $(o\text{-}TP)_2{}^-$ measured at 1064 nm. The spectra including a shoulder peak of $CNBP^-$ were deconvoluted using a set of Gaussian functions.

$(BP)_2{}^-$, $(o\text{-}TP)_2{}^-$, and $(m\text{-}TP)_2{}^-$ were determined to be 0.13,[9] 0.28, and 0.28 eV, respectively. The incremental rate of EA_a (or vertical detachment energy) from monomer anion to dimer anion is ca. 0.3 eV in common for p-TP[10] and similar-sized aromatic hydrocarbons such as naphthalene,[11] anthracene,[12] and pyrene.[7b] Thus, the EA_a of the monomer can be estimated to be ca. −0.17 eV for BP and ca. −0.02 eV for o- and m-TPs.

The deconvolution of the spectra using a set of Gaussian functions reveals that there is a common vibrational structure having an energy spacing of 0.16 eV (ca. 1290 cm^{-1}) in all the spectra (see Figure 1). This energy is in good agreement with the frequency of the (in-phase) inter-ring CC stretching vibration of the oligophenyl compounds (1280–1300 cm^{-1}),[12–14] so that this vibrational feature is assignable to this mode. Since the lowest unoccupied molecular orbitals (LUMO) of the oligophenyls possess high electron density on the inter-ring CC bonds, the inter-ring CC bond lengths are largely shortened on going from the neutral to anion.[14] Hence, the observed vibrational features confirm the formation of valence radical anions of oligophenyls in the gas phase. Furthermore, the experimental EA_a values determined in the present study indeed agree well with the calculated EA_a of the valence state oligophenyl anions (see Table 1).

We anticipate that the present EA_a data of the isolated oligophenyl molecules will be useful to estimate polarization energy for anion as well as electron-transport energy level in the oligophenyl solid materials.

Table 1. Experimental and calculated adiabatic electron affinities (EA_a)

Compound	Exptl. EA_a/eV	Theoretical EA_a/eV[a]
biphenyl (BP)	≈−0.17	−0.18 (−0.04)
4-cyanobiphenyl (CNBP)	0.72 ± 0.01	0.73 (0.83)
o-terphenyl (o-TP)	≈−0.02	0.003 (0.14)
m-terphenyl (m-TP)	≈−0.02	0.063 (0.21)
p-terphenyl (p-TP)	0.39 ± 0.01	0.33 (0.45)
p-quaterphenyl (p-QP)	0.66 ± 0.02	0.61 (0.73)
1,3,5-triphenylbenzene (TPB)	0.30 ± 0.02	0.19 (0.36)

[a] The zero-point vibrational energy corrected EA_a are listed in parentheses.

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8 It is expected that there are several energetically close conformers for each oligophenyl. Indeed, two stable conformers exist for m-TP: a helical conformation gauche$^+$–gauche$^+$–gauche$^+$ with respect to the inter-ring CC bond and a twisted conformation gauche$^+$–gauche$^-$–gauche$^+$. However, we neglect such structural difference, because the energy differences between these conformers are less than 10 meV, which is not discernible due to the limited energy-resolution of our spectrometer (ca. 50 meV).
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