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## A: Spectroscopy, Molecular Structure, and Quantum Chemistry

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## **Dissociative Electron Attachment to 2,3,6,7,10,11-Hexabromotriphenylene**

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### Abstract

2,3,6,7,10,11-Hexabromotriphenylene (HBTP) and 2,3,6,7,10-pentabromotriphenylene (PBTP) were investigated by means of Dissociative Electron Attachment Spectroscopy (DEAS). The dominant decay channel of the transient molecular negative ions consists in elimination of Br<sup>-</sup> with resonances in the low electron energy region. Formation of long-lived parent anions with autodetachment lifetime  $\tau_a$ =310 µs is observed at thermal electron energies. The adiabatic electron affinities,  $EA_a$ =1.12±0.1 eV in HBTP and 1.09±0.1 eV in PBTP, evaluated using a simple Arrhenius approach are in good agreement with those predicted by DFT (XYG3/Def2-TZVPP//PBE0/Def2TZVPP) calculations.

## Introduction

Over the past decade, polyhalogenated polyaromatic hydrocarbons received considerable attention as precursors for the synthesis of various polyaromatic systems,<sup>1</sup> graphene-like films,<sup>2</sup> carbon nanobelts,<sup>3,4</sup> graphene nanoribbons,<sup>5</sup> covalent polymers frameworks (COFs),<sup>6–9</sup> disk- and star-shaped molecules,<sup>10,11</sup> and other molecular materials for optoelectronics, catalysis, energy

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storage, and gas separation. Transition-metal-catalyzed cross-coupling reactions<sup>12-14</sup> enable highly efficient and selective functionalization of polyhalogenated polyaromatic hydrocarbons at their peripheral sites. Among polyhalogenated polyaromatic hydrocarbons, 2,3,6,7,10,11hexabromotriphenylene (HBTP) is one of the most common and readily available <sup>15</sup> building blocks for the synthesis of star-shaped molecules, discotic liquid crystals, <sup>10,13,16,17</sup> and twodimensional  $\pi$ -conjugated COFs <sup>8,9</sup>. Recent studies of the aryl-aryl coupling of HBTP on the Au(111) surface by means of scanning transmission electron microscopy (STEM) and density functional theory (DFT) simulations revealed four possible reaction pathways depending on the reaction temperature and post-annealing temperature <sup>18</sup>. Obviously, these reactions are largely controlled by the electron-transfer processes and, therefore, by the electron affinity of HBTP and stability of its anion-radical. Surprisingly, no data have been reported so far regarding the electron affinity of HBTP. In contrast to triphenylene and its hexaalkyl derivatives, 19,20,15,10 electrochemical studies of HBTP are impeded by its low solubility in organic solvents. However, HBTP shows high thermal stability and can be transferred into the gas phase without decomposition or isomerization at the temperatures of 225–270 °C<sup>21</sup>. Here we report the first study of dissociative electron attachment to HBTP in the gas phase. We report the major decay channels of its molecular negative ion and its gas-phase electron affinity.

#### **Experiment and Calculations**

#### Materials and methods

Triphenylene (98%, Sigma-Aldrich), bromine (reagent grade, Sigma-Aldrich), reduced iron fine powder (99+%, Sigma-Aldrich), nitrobenzene (99+% Sigma-Aldrich), *o*-dichlorobenzene (99%, Abcr), dichloromethane (99.9%, Chimmed, Russia), diethyl ether (analytical grade, Chimmed, Russia) were used as received without further purification. Toluene (99%, Chimmed, Russia) used for HPLC–MS analysis was purified by refluxing in the presence of Na under inert atmosphere followed by distillation.

HPLC–UV/Vis and HPLC–MS analyses were performed in parallel using an Agilent 1100 series/DAD/6410 triple quad LC/UV-Vis/MS system, equipped with a Cosmosil Buckyprep column (4.6 mm I.D. × 25 cm, thermostated at 23 °C), diode-array detector (DAD operated within 190–950 nm wavelength range with 2 nm resolution), and atmospheric-pressure photoionization (APPI) ion source (positive ion mode). Toluene at a flow rate of 1 ml min<sup>-1</sup> was taken as an eluent, the void volume being 3.0 ml. IR spectra were registered within the wavenumber range of 400–4000 cm<sup>-1</sup> (KBr tablet, resolution of 2 cm<sup>-1</sup>) using FT-IR IRAffinity-1 spectrometer (Shimadzu, Japan). The absorption spectra were recorded with the use of the AvaSpec-ULS2048x64TEC-USB2 Sensline fiber-optic spectrometer with a cooled, back-thinned detector (spectral range 200–1160 nm, optical resolution 1.2 nm, enhanced sensitivity in the UV and IR regions, Avantes, Netherlands) equipped with the AvaLight-DH-S-Bal light source (190–2500 nm range, deuterium and halogen lamps, Avantes, Netherlands). The samples dissolved in o-DCB or dichloromethane were measured in a cuvette with optical path length of 10 mm.

#### Synthetic procedure

Synthesis of 2,3,6,7,10,11-hexabromotriphenylene (HBTP) was performed as described elsewhere <sup>15</sup>. Fe powder (0.18 g) was added into the mixture of triphenylene (2 g, 8.8 mmol) and nitrobenzene (80 ml) at room temperature followed by the dropwise addition of bromine (4 ml) over 5 min. Next, the solution was stirred at room temperature during 10 h, and then heated under reflux (205°C) during 2 h. Upon heating, dissolution of the solid material and vigorous evolution of HBr gas took place. Next, the reaction mixture was cooled down to room temperature, diethyl ether (200 ml) was added, and the precipitate was filtered off. The resulted greyish powder was recrystallized from *o*-dichlorobenzene (800 ml) to give the target product (5.6 g, 92%) as light grey powder limitedly soluble in most of common organic solvents. The product was identified according to IR, UV-Vis, and HPLC–MS data as 2,3,6,7,10,11-hexabromotriphenylene (HBTP) with 95% purity, 5% impurity attributed to 2,3,6,7,10-pentabromotriphenylene (PBTP).

2.3,6,7,10,11-hexabromotriphenylene (HBTP) FT-IR (KBr disc, 2 cm<sup>-1</sup>), v / cm<sup>-1</sup>: 419 (w), 427 (m), 525 (m), 605 (vw), 622 (vw), 657 (m), 701 (w), 769 (vw), 814 (w), 864 (vs), 873 (vs), 922 (vw), 965 (vw), 1026 (w), 1119 (s), 1193 (w), 1226 (vw), 1234 (vw), 1283 (w), 1324 (w), 1340 (w), 1366 (vs), 1454 (vs), 1468 (w), 1473 (w), 1480 (w), 1507 (vw), 1553 (m), 1586 (m), 1732 (w). UV/Vis (dichlorometane),  $\lambda_{max}$  / nm: 267, 272 (sh), 277, 288 (sh), 303, 308 (sh), 321 (sh), 331 (sh), 346, 352, 363 (sh). UV/Vis (*o*DCB),  $\lambda_{max}$  / nm: 308, 310 (sh), 324 (sh), 346 (sh), 352, 364. HPLC-MS (Cosmosil Buckyprep 4.6 mm I.D. × 25 cm, toluene, 1 ml min<sup>-1</sup>, 23 °C, PI APPI, TIC),  $t_R$ /min: 8.7 (5%, C<sub>18</sub>H<sub>7</sub>Br<sub>5</sub>) and 12.9 (95%, C<sub>18</sub>H<sub>6</sub>Br<sub>6</sub>). APPI MS (positive ion mode), *m/z*: 701.6 (C<sub>18</sub>H<sub>6</sub>Br<sub>6</sub><sup>+</sup>, M<sup>+</sup>, 100%).

<u>2,3,6,7,10-pentabromotriphenylene (PBTP)</u> HPLC–MS (Cosmosil Buckyprep 4.6 mm I.D. × 25 cm, toluene, 1 ml min<sup>-1</sup>, 23 °C, PI APPI, TIC),  $t_{\rm R}$  / min: 8.7. APPI MS (positive ion mode), m/z: 621.6 (C<sub>18</sub>H<sub>7</sub>Br<sub>5</sub><sup>+</sup>,  $M^+$ , 100%).

*Triphenylene* HPLC–MS (Cosmosil Buckyprep 4.6 mm I.D. × 25 cm, toluene, 1 ml min<sup>-1</sup>, 23 °C, PI APPI, TIC),  $t_{\rm R}$  / min: 3.41. APPI MS (positive ion mode), m/z: 288.1 (C<sub>18</sub>H<sub>12</sub><sup>+</sup>,  $M^+$ , 100%). UV/Vis (dichloromethane),  $\lambda_{\rm max}$  / nm: 259, 273 (sh), 286, 302 (sh), 314 (sh), 322, 329, 336, 345 (sh). UV/Vis (*o*DCB),  $\lambda_{\rm max}$  / nm: 305 (sh), 323, 330, 337, 345 (sh).

#### DEAS measurements

The negative ion (NI) mass spectrometer used in this work has been described previously.<sup>22</sup> A magnetically collimated electron beam is passed through vapors of the compounds measured under single-collision conditions. The negative ions thus formed are electrostatically extracted from the collision cell and subsequently mass-analyzed by a magnetic sector instrument. Their current is measured by a secondary electron multiplier as a function of the incident electron energy. The accessible electron energy range is 0-15 eV, and the electron energy scale is calibrated using the zero-energy SF<sub>6</sub><sup>---</sup> reference signal that results from thermal electron capture by SF<sub>6</sub>. Since an electron energy monochromator was absent, the full width at half-maximum

(fwhm) of the incident electron energy distribution is estimated as 0.4 eV. The incident electron beam current is typically 1  $\mu$ A, the accuracy of the measured peak energy being ±0.1 eV.

Measurements of the electron autodetachment lifetime are based on detecting a beam of neutral autodetachment products formed in the free drift region between the mass analyzer and the secondary electron multiplier, and include two steps. Firstly, the total beam of charged and neutral species is measured. Secondly, the negative ions are deflected by a pair of deflectors set up in front of the entrance slit of multiplier, and, thus, only the beam of neutral species is detected. The NI lifetime  $\tau_a$ , assuming an exponential NI decay, can be evaluated by the formula:

$$\tau_a = -\frac{t_0}{\ln\left(1 - \frac{l_n}{I}\right)},\tag{1}$$

where  $t_0$  is the anion drift time between the magnetic mass analyzer and the secondary electron multiplier,  $I_n$  is the current of the neutral species, and I is the total current of the neutral and the charged components of the beam.<sup>22</sup> This method has been originally used with a time-of-flight setup,<sup>23</sup> and later it was implemented by Khvostenko et al. with a magnetic mass analyser.<sup>24</sup> A typical timing for m/z= 146 (SF<sub>6</sub><sup>--</sup> reference) is as follows. Under typical experimental conditions, the extraction of ions from the collision cell (ionization chamber) occurs in ~10 µs. Then, acceleration of the ions and their subsequent passage through the first free drift region take ~6 µs at the acceleration energy of 4 keV. Passage through the mass analyzer before entering the second free drift region takes further 6 µs. Only the autodetachment products, which are formed within yet further 6 µs of flight through the second drift region, can reach the detector and be measured. Vorob'ev et al. recommended that the electron autodetachment measurements are to be referenced against SF<sub>6</sub><sup>--</sup> under particular well-defined experimental conditions.<sup>25</sup> In our experimental apparatus,  $\tau_a(SF_6^{--}) = 150$  µs, at the collision cell temperature of 70 °C.<sup>26</sup>

The lifetime measurements for the molecular negative ions are known to give fairly accurate estimates of the adiabatic electron affinity (EA<sub>*a*</sub>) within the error limits of  $\pm 0.1$  eV <sup>27,28</sup> through the use of the equation:

$$\tau_a = \tau_0 \cdot exp \left[ \frac{N \cdot EA_a}{EA_a + Nk_B T + \varepsilon} \right]$$
(2).

Here,  $\tau_0$ , the inverse of the frequency factor, represents the characteristic time of motion along the reaction coordinate (relaxation of the anionic geometry to that of the neutral molecule upon autodetachment), *N*=3*n*-6 is the number of the internal degrees of freedom, *k*<sub>B</sub> is the Boltzmann constant, *T* is the temperature of the target molecule (ionization chamber temperature), and  $\varepsilon$  is the kinetic energy of incoming electrons. The value of  $\tau_0$  depends on the exact structure of the anion and may vary from 10<sup>-13</sup> s for the naphthoquinone derivatives<sup>27</sup> to 5·10<sup>-13</sup> s for the benzene derivatives.<sup>28</sup>

#### Quantum chemical calculations.

Density functional theory (DFT) calculations were performed with the Firefly software<sup>29</sup> partly based on the GAMESS(US) source code.<sup>30</sup> The geometry optimization of the species involved and computation of the ZPE correction (scaled by 0.97) were done at the PBE0/Def2-TZVPP level of theory. The electronic energy was then recomputed with the use of the XYG3 double hybrid functional <sup>31</sup> and the same Def2-TZVPP basis set. The theoretical appearance thresholds were calculated as the respective combinations of the ZPE-corrected XYG3 results. We observed that addition of the diffuse functions causes instabilities in the SCF convergence due to proximity of the basis set to linear dependence (even when applied to the bromine atoms only) while providing no appreciable improvement of the computational results.

#### **Results and discussion**

2,3,6,7,10,11-Hexabromotriphenylene (HBTP,  $C_{18}H_6Br_6$ ) was synthesized according to the previous work.<sup>15</sup> Electrophilic aromatic bromination of triphenylene occurs regioselectively and yields HBTP as the main product, which can be purified by recrystallization from the hot *o*-dichlorobenzene. Its positive ion APPI mass spectrum is constituted by the  $C_{18}H_6Br_6^+$  molecular ion, the observed isotopic pattern being in agreement with the theoretical one (Fig. 1*a*).

 According to the HPLC–MS(APPI) data (*SI*, Fig. *S2a*), the isolated HBTP was 95% pure, contaminated with 2,3,6,7,10-pentabromotriphenylene (PBTP, 5%, *SI*, Fig. *S2b*).

UV-Vis and IR spectra of the product are in good agreement with the literature data (Fig. 1*b* and *S*1 in *SI*).<sup>21,32</sup> The electronic spectra demonstrate that bromination of triphenylene redshifts the intense bands of the  $\pi$ - $\pi$ \* transitions by ca 0.2–0.3 eV as a result of partial conjugation between the  $\pi$ -aromatic system and the lone pairs of bromine atoms (Fig. 1*b*). The optical gaps  $E_{\rm G}$  for triphenylene and HBTP were estimated to be 3.4 and 3.3 eV, respectively.

Triphenylene has already been investigated by means of DEAS.<sup>33,34</sup> Only the dehydrogenated fragment anion [M–H]<sup>-</sup> was detected at 8 eV with a weak shoulder at ca. 4.5 eV. No long-lived (>10 µs) parent anion was found. This observation is not surprising since the  $EA_a$  of triphenylene is rather low, most likely in the range of 0.14–0.29 eV <sup>35–37</sup>. Using eq. (2), one can estimate the lifetime of the triphenylene anion ( $\tau_a$ ) to be below 7 µs at the ionization chamber temperature of ~90 °C. All the transient anions with  $\tau_a$  shorter than 10 µs are not detectable with our experimental setup.<sup>24</sup> Indeed, the drift time of the triphenylene anion ( $C_{18}H_{12}^{--}$ , m/z=228) between its formation and detection is about 28 µs ×  $\sqrt{228/146} = 35$  µs, where 28 µs is the drift time of SF<sub>6</sub><sup>--</sup> (m/z=146).

The results of DEAS measurements in HBTP and PBTP are presented in Fig. 2 and Table 1. The long-lived molecular anions of HBTP and PBTP were found in the spectra (Fig 2*a*, *b*). The main decay channel of the transient molecular anion of HBTP consists in detachment of Br<sup>-</sup> peaked at nearly thermal energy (0.06 eV, Fig. 2*c*). Weak additional resonances are observed at 2.8, 3.7 and 5.6 eV. Metastable ions  $m^*$  with apparent m/z 8.94 ( $m^*=m^2/M$ , where *m* and *M* are the masses of the fragment anion and the parent anion, respectively), detected at thermal electron energy, directly confirm that the dissociation occurs on the microsecond timescale,<sup>38</sup> in agreement with our observation of the long-lived fraction of C<sub>18</sub>H<sub>6</sub>Br<sub>6</sub><sup>-</sup> molecular anions (Fig. 2*a*). By measuring the lifetimes of molecular anions with respect to electron autodetachment, one can quantify the *EA*<sub>a</sub> of the molecule itself using the following inversion of the Eq. (2):<sup>25,39</sup>

$$EA_{a} = \frac{ln\left(\frac{\tau_{a}}{\tau_{0}}\right) \cdot (NkT + \varepsilon)}{N - ln\left(\frac{\tau_{a}}{\tau_{0}}\right)}$$
(3).

This procedure was also done for PBTP using the signal of its molecular negative ion  $C_{18}H_7Br_5^-$  (Fig. 2*b* and Table 1). Good agreement between the experimental and DFT-calculated values of the electron affinity corroborates the adequacy of our estimates.

#### Conclusions

2,3,6,7,10,11-Hexabromotriphenylene was investigated by means of Dissociative Electron Attachment Spectroscopy (DEAS). The dominant dissociative decay channel of the transient molecular negative ions leads to formation of Br<sup>-</sup> in the low electron energy region. Formation of the long-lived parent anions is observed at thermal electron energies, the autodetachment lifetime being 310  $\mu$ s. The adiabatic electron affinity,  $EA_a=1.12\pm0.1$  eV, was evaluated using a simple Arrhenius approximation. For the C<sub>18</sub>H<sub>7</sub>Br<sub>5</sub> impurity, a close  $EA_a$  estimate of 1.09±0.1 eV was obtained. Both values are in good agreement with the results of DFT calculations.

#### Supporting Information

The IR spectrum, HPLC-MS and DEAS data for HBTP as well as HPLC–UV/Vis–MS data for triphenylene are the content of the file supplied as Supporting Information (SI).

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## References

- (1) Majewski, M. A.; Stępień, M. Bowls, Hoops, and Saddles: Synthetic Approaches to Curved Aromatic Molecules. *Angew. Chem. Int. Ed.* **2019**, *58*, 86–116.
- (2) Kudaş, Z.; Gür, E.; Ekinci, D. Synthesis of Graphene-like Films by Electrochemical Reduction of Polyhalogenated Aromatic Compounds and Their Electrochemical Capacitor Applications. *Langmuir* **2018**, *34*, 7958–7970.
- (3) Cheung, K. Y.; Gui, S.; Deng, C.; Liang, H.; Xia, Z.; Liu, Z.; Chi, L.; Miao, Q. Synthesis of Armchair and Chiral Carbon Nanobelts. *Chem* **2019**, *5*, 838–847.
- (4) Segawa, Y.; Levine, D. R.; Itami, K. Topologically Unique Molecular Nanocarbons. *Acc. Chem. Res.* **2019**, *52*, 2760–276.
- (5) Sisto, T. J.; Zhong, Y.; Zhang, B.; Trinh, M. T.; Miyata, K.; Zhong, X.; Zhu, X.-Y.; Steigerwald, M. L.; Ng, F.; Nuckolls, C. Long, Atomically Precise Donor–Acceptor Cove-Edge Nanoribbons as Electron Acceptors. J. Am. Chem. Soc. 2017, 139, 5648–5651.
- (6) Jin, S.; Furukawa, K.; Addicoat, M.; Chen, L.; Takahashi, S.; Irle, S.; Nakamura, T.; Jiang, D. Large Pore Donor–Acceptor Covalent Organic Frameworks. *Chem. Sci.* 2013, 4, 4505.
- (7) Lohse, M. S.; Bein, T. Covalent Organic Frameworks: Structures, Synthesis, and Applications. *Adv. Funct. Mater.* **2018**, *28*, 1705553.
- Ye, X.-L.; Huang, Y.-Q.; Tang, X.-Y.; Xu, J.; Peng, C.; Tan, Y.-Z. Two-Dimensional Extended π-Conjugated Triphenylene-Core Covalent Organic Polymer. J. Mater. Chem. A 2019, 7, 3066–3071.
- (9) Guo, J.; Xu, Y.; Jin, S.; Chen, L.; Kaji, T.; Honsho, Y.; Addicoat, M. A.; Kim, J.; Saeki, A.; Ihee, H.; Seki, S.; Irle, S.; Hiramoto, M.; Gao, J.; Jiang, D. Conjugated Organic Framework with Three-Dimensionally Ordered Stable Structure and Delocalized π Clouds. *Nat. Commun.* 2013, *4*, 2736.
- (10) Wang, D.; Mi, Y.; Tang, J.; Liang, P.; Jin, Z.; Yang, Z.; Yang, H. Disk-Shaped Symmetric Hexa-Substituted Triphenylene Derivatives: Synthesis, Physical Properties and Self-Assembly. *Chem. Res. Chin. Univ.* **2013**, *29*, 495–499.
- (11) Zhang, H.; Wu, D.; Hua Liu, S.; Yin, J. Star-Shaped Polycyclic Aromatic Hydrocarbons: Design and Synthesis of Molecules. *Curr. Org. Chem.* **2012**, *16*, 2124–2158.
- (12) Diab, H. M.; Abdelmoniem, A. M.; Shaaban, M. R.; Abdelhamid, I. A.; Elwahy, A. H. M. An Overview on Synthetic Strategies for the Construction of Star-Shaped Molecules. *RSC Adv.* 2019, *9*, 16606–16682.
- (13) de Meijere, A.; Stulgies, B.; Albrecht, K.; Rauch, K.; Wegner, H. A.; Hopf, H.; Scott, L. T.; Eshdat, L.; Aprahamian, I.; Rabinovitz, M. New Interesting Molecular Topologies by Way of Modern Cross-Coupling Reactions. *Pure Appl. Chem.* 2006, 78, 813–830.
- (14) Stulgies, B.; Prinz, P.; Magull, J.; Rauch, K.; Meindl, K.; Rühl, S.; de Meijere, A. Six- and Eightfold Palladium-Catalyzed Cross-Coupling Reactions of Hexa- and Octabromoarenes. *Chem. Eur. J.* 2005, *11*, 308–320.
- (15) Breslow, R.; Jaun, B.; Kluttz, R. Q.; Xia, C. Ground State Pi-Electron Triplet Molecules of Potential Use in the Synthesis of Organic Ferromagnets. *Tetrahedron* 1982, *38*, 863– 867.
- (16) Chen, L.; Kim, J.; Ishizuka, T.; Honsho, Y.; Saeki, A.; Seki, S.; Ihee, H.; Jiang, D. Noncovalently Netted, Photoconductive Sheets with Extremely High Carrier Mobility and Conduction Anisotropy from Triphenylene-Fused Metal Trigon Conjugates. *J. Am. Chem. Soc.* 2009, *131*, 7287–7292.
- (17) Krempl, H.; Mattmer, R.; Hanack, M. Synthesis of Hexacyanotriphenylene and Hexacyanotribenzylene. *Synthesis* **2000**, *2000*, 1705–1708.
- (18) Zhang, R.; Xia, B.; Xu, H.; Lin, N. Kinetically Controlled Synthesis of Four- and Six-Member Cyclic Products via Sequential Aryl-Aryl Coupling on a Au(111) Surface. *ChemPhysChem* 2019, 20, 2292–2296.

- (19) Peover, M. E.; White, B. S. The Electro-Oxidation of Polycyclic Aromatic Hydrocarbons in Acetonitrile Studied by Cyclic Voltammetry. J. Electroanal. Chem. Interfacial Electrochem. 1967, 13, 93–99.
- (20) Meerholz, K.; Heinze, J. Multiple Reversible Electrochemical Reduction of Aromatic Hydrocarbons in Liquid Alkylamines. J. Am. Chem. Soc. **1989**, 111, 2325–2326.
- (21) Song, W.; Martsinovich, N.; Heckl, W. M.; Lackinger, M. Thermodynamics of Halogen Bonded Monolayer Self-Assembly at the Liquid–Solid Interface. *Chem Commun* 2014, 50, 13465–13468.
- (22) Pshenichnyuk, S. A.; Vorob'ev, A. S.; Modelli, A. Resonance Electron Attachment and Long-Lived Negative Ions of Phthalimide and Pyromellitic Diimide. J. Chem. Phys. 2011, 135, 184301.
- (23) Edelson, D.; Griffiths, J. E.; McAfee, K. B. Autodetachment of Electrons in Sulfur Hexafluoride. *J. Chem. Phys.* **1962**, *37*, 917–918.
- (24) Khvostenko, V. I. Negative Ion Mass Spectrometry in Organic Chemistry; Nauka: Moscow, 1980.
- (25) Asfandiarov, N. L.; Pshenichnyuk, S. A.; Rakhmeyev, R. G.; Tuktarov, R. F.; Zaitsev, N. L.; Vorob'ev, A. S.; Kočišek, J.; Fedor, J.; Modelli, A. 4-Bromobiphenyl: Long-Lived Molecular Anion Formation and Competition between Electron Detachment and Dissociation. J. Chem. Phys. 2019, 150, 114304.
- (26) Vorob'ev, A. S.; Asfandiarov, N. L.; Lukin, V. G.; Lomakin, G. S. Multiexponential Decay of Negative Molecular Ions as a Result of Target Molecule Distribution over Vibrational States. *Tech. Phys.* **2009**, *54*, 1255–1262.
- (27) Asfandiarov, N. L.; Pshenichnyuk, S. A.; Vorob'ev, A. S.; Nafikova, E. P.; Elkin, Y. N.; Pelageev, D. N.; Koltsova, E. A.; Modelli, A. Electron Attachment to Some Naphthoquinone Derivatives: Long-Lived Molecular Anion Formation: Electron Attachment to Some Naphthoquinone Derivatives. *Rapid Commun. Mass Spectrom.* 2014, 28, 1580–1590.
- (28) Asfandiarov, N. L.; Pshenichnyuk, S. A.; Vorob'ev, A. S.; Nafikova, E. P.; Modelli, A. Electron Affinity Evaluation for Nitrobenzene Derivatives Using Negative Ion Lifetime Data: Electron Affinity Evaluation for Nitrobenzene Derivatives. *Rapid Commun. Mass Spectrom.* 2015, 29, 910–912.
- (29) Granovsky, A. A. Firefly v. 8.2.0 (Formerly PC GAMESS); 2016.
- (30) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. General Atomic and Molecular Electronic Structure System. *J. Comput. Chem.* **1993**, *14*, 1347–1363.
- (31) Zhang, Y.; Xu, X.; Goddard, W. A. Doubly Hybrid Density Functional for Accurate Descriptions of Nonbond Interactions, Thermochemistry, and Thermochemical Kinetics. *Proc. Natl. Acad. Sci.* **2009**, *106*, 4963–4968.
- (32) Hirose, T.; Miyazaki, Y.; Watabe, M.; Akimoto, S.; Tachikawa, T.; Kodama, K.;
  Yasutake, M. Trialkylsilylethynyl-Substituted Triphenylenes and Hexabenzocoronenes: Highly Soluble Liquid Crystalline Materials and Their Hole Transport Abilities. *Tetrahedron* 2015, *71*, 4714–4721.
- (33) Khatymov, R. V.; Tuktarov, R. F.; Muftakhov, M. V. Lifetime of Negative Molecular Ions of Tetracene and Pentacene with Respect to the Autodetachment of an Electron. *JETP Lett.* **2011**, *93*, 437–441.
- (34) Muftakhov, M. V.; Khatymov, R. V.; Tuktarov, R. F. Decomposition of Aromatic Compounds Relevant to Organic Electronics under Exposure to Low-Energy Electrons. *Tech. Phys.* **2018**, *63*, 1854–1860.
- (35) Wentworth, W. E.; Becker, R. S. Potential Method for the Determination of Electron Affinities of Molecules: Application to Some Aromatic Hydrocarbons. J. Am. Chem. Soc. 1962, 84, 4263–4266.

- (36) Becker, R. S.; Chen, E. Extension of Electron Affinities and Ionization Potentials of Aromatic Hydrocarbons. *J. Chem. Phys.* **1966**, *45*, 2403–2410.
- (37) Tanner, D. D.; Deonarian, N.; Kharrat, A. Electron Affinities and Marcus Reorganization Energies. A Correlation between Gas Phase Electron Affinities and Solution Phase Redox Potentials. *Can. J. Chem.* **1989**, *67*, 171–175.
- (38) Beynon, J. H. *Mass Spectrometry and It Applications to Organic Chemistry*; Elsevier: Amsterdam-London-New-York-Princeton, 1960.
- (39) Asfandiarov, N. L.; Muftakhov, M. V.; Pshenichnyuk, S. A.; Papp, P.; Danko, M.; Lacko, M.; Blaško, J.; Matejčik, Š.; Modelli, A. Dissociative Electron Attachment to 2,4,6-Trichloroanisole and 2,4,6-Tribromoanisole Molecules. *J. Chem. Phys.* 2017, 147, 234302.

### Table 1.

Negative ions observed in the DEA spectra of HBTP, lifetimes and  $EA_a$  for HBTP and PBTP, as well as thermodynamic appearance threshold for the Br<sup>-</sup> fragment ion.

Anion					EA <sub>a</sub> / eV	
m/z	Assignment	Peak energy, eV	Intensity, %	Lifetime, µs	Lifetime-based estimates	DFT
702	HBTP-	0.0	36.6	310	1.12±0.1	1.18
79	Br <sup>-</sup>	0.06 <sup>[a]</sup>	100	_	-	$0.34^{[b]}$
8.94 <sup>[c]</sup>	HBTP*⁻→Br⁻	0.04	0.1	_	_	_
622	PBTP-	0.0	1.0	196	$1.09 \pm 0.1$	1.12

[a] Weak additional resonances were observed at energies of 2.8 (1.3%), 3.7 (1.3%), 5.6 (shoulder, 1.0%) eV. [b] Thermodynamic appearance threshold for the Br<sup>-</sup> fragment ion. [c] Metastable ion.

# **Figure Captions**

**Figure 1.** (*a*) PI APPI mass spectrum of HBTP (molecular structure, theoretical and experimental isotopic abundances of HBTP are shown in insets). (*b*) UV-Vis spectra of HBTP and triphenylene in dichloromethane and *o*DCB (inset, 300–400 nm) solutions.

**Figure 2.** NI effective yield curves and molecular anion lifetimes for (*a*) HBTP, (*b*) PBTP, and (*c*) Br<sup>-</sup> fragment ion as a function of incident electron energy; (*d*) electron energy distribution from reference gas  $SF_6^{-}/SF_6$ .



Figure 1. (a) PI APPI mass spectrum of HBTP (molecular structure, theoretical and experimental isotopic abundances of HBTP are shown in insets). (b) UV-Vis spectra of HBTP and triphenylene in dichloromethane and *o*DCB (inset, 300–400 nm) solutions.



Figure 2. NI effective yield curves and molecular anion lifetimes for (a) HBTP, (b) PBTP, and (c) Br<sup>-</sup> fragment ion as a function of incident electron energy; (d) electron energy distribution from reference gas  $SF_6^{-\bullet}/SF_6$ .



63x47mm (300 x 300 DPI)