

Electronic Supplementary Information (ESI) for

**Gas-Phase Preparation of the Dibenzo[*e,l*]pyrene (C₂₄H₁₄) Butterfly Molecule
via a Phenyl Radical Mediated Ring Annulation**

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1. Experimental Methods

The experiments were conducted at the X04DB beamline of the Swiss Light Source (SLS) at the Paul Scherrer Institute (PSI) utilizing a molecular beam apparatus coupled to a resistively heated silicon–carbide (SiC) chemical microreactor, which was operated with a double velocity map imaging (VMI) photoelectron photoion coincidence spectrometer.¹ Elementary reactions of pyrolytically generated phenyl ($C_6H_5^*$) radicals are explored *in situ* to investigate the molecular mass growth processes of aromatic molecules. Briefly, nitrosobenzene (C_6H_5NO ; 97%, Sigma-Aldrich) was placed in a glass bubbler and seeded at a fraction of less than 1 % in helium (He; 99.996 %, PanGas) at a backing pressure of 150 mbar. The gas mixture passed through a high-vacuum oven where triphenylene ($C_{18}H_{12}$; 98%, Sigma-Aldrich) was sublimed at 423 ± 1 K and incorporated into the gas mixture, which exited the oven through a 200 μ m diameter nozzle into a SiC tube with 20 mm heated length and 1 mm inner diameter. Phenyl radicals ($C_6H_5^*$) were generated *in situ* via pyrolysis of nitrosobenzene at a reactor temperature of $1,200 \pm 100$ K measured by a type C thermocouple. Products formed attain supersonic expansion upon leaving the reactor and pass through a 2 mm diameter skimmer into the experimental chamber where the photoelectron photoion coincidence (PEPICO) spectrometer resides. Here, quasi-continuous synchrotron vacuum ultraviolet (VUV) radiation tuned from 7.00–10.00 eV is exploited to ionize reaction products under fragment-free soft ionization conditions.² A constant electric field of 218 $V\text{ cm}^{-1}$ was used to extract both the cations and electrons in opposite directions to be velocity map imaged on separate position-sensitive delay-line anode detectors (Roentdek DLD40). Data obtained include photoionization efficiency (PIE) curves, which depict ion counts as a function of photon energy at a specific mass-to-charge ratio (m/z), and mass-selective threshold photoelectron (ms-TPE) spectra, which are collected from the same method as the PIE curves whilst selecting only the photoelectrons with kinetic energy less than 10 meV in coincidence with photoions at the desired m/z . The procedure of Sztaray et al.³ was used to subtract the hot electron signal from the threshold (kinetic energy less than 10 meV) electrons. Selecting only the room temperature background in the VMI for the ions results in a reduction in spectral broadening and hot bands from insufficient cooling of the molecular beam.⁴ Calibration curves for dibenzo[*e,l*]pyrene ($C_{24}H_{14}$; 99.2 %, PAH Research) for comparison to the conducted reaction were obtained using an effusive oven source heated to 100–150° C.⁵

2. Computational Methods

The GAUSSIAN 16⁶ program was used to explore the synthetic pathways to dibenzo[*e,l*]pyrene via electronic structure calculations. The reactants, products, intermediates, and transition states along these reaction pathways were identified and characterized. Density functional theory at the B3LYP⁷/cc-pVTZ level was used to optimize geometries and harmonic frequencies, and the energies were refined by coupled cluster⁸ CCSD(T)/cc-pVDZ with B3LYP/cc-pVTZ zero-point energy corrections. Franck-Condon simulations are based on geometry optimizations and harmonic frequency calculations at the (TD)B3LYP/6-311++G(d,p) levels of theory. The stick spectra have been calculated using the ezSpectrum suit of programs in the Dushinsky approximations at 300 K and were convoluted by 100–120 meV gaussian functions to match with the experimental data.⁹

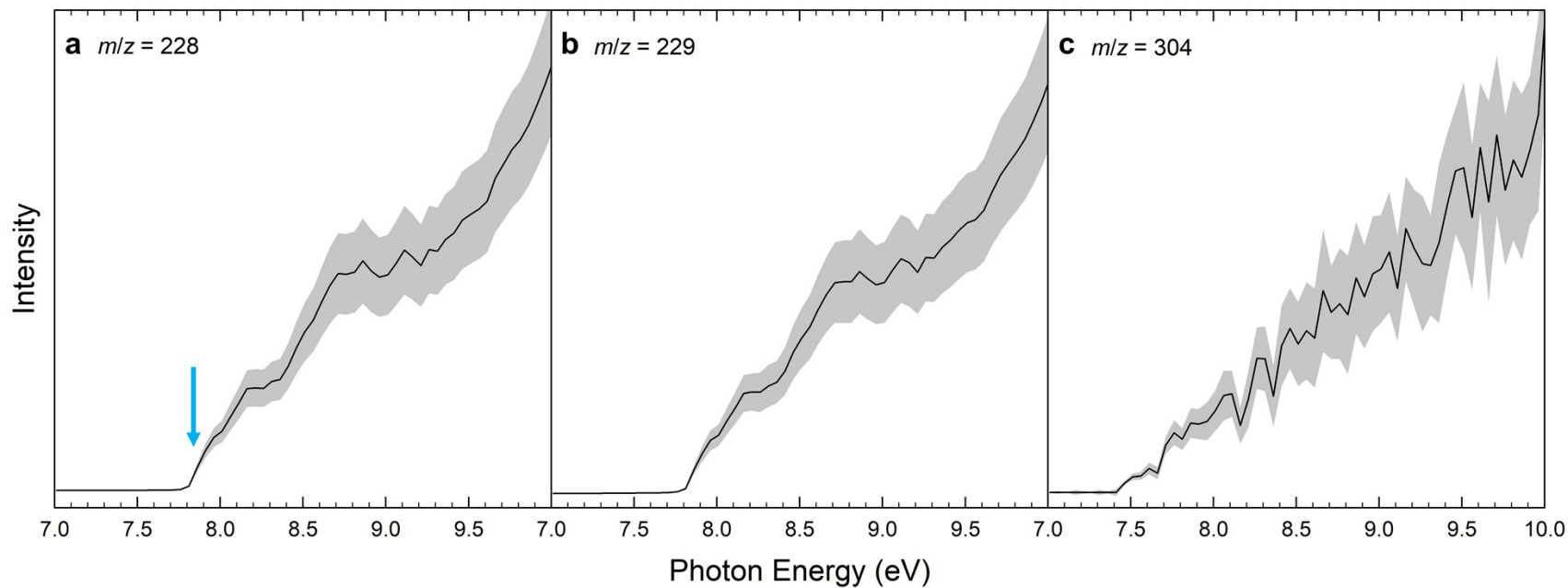


Fig. S1 Photoionization efficiency (PIE) curves for the nitrosobenzene (C_6H_5NO) – triphenylene ($C_{18}H_{12}$) system at (a) $m/z = 228$ ($C_{18}H_{12}$), (b) $m/z = 229$ ($^{13}CC_{17}H_{12}$), and (c) $m/z = 304$ ($C_{24}H_{16}$). The overall error bars (gray area) consist of two parts: 1σ error of the PIE curve averaged over the individual scans and $\pm 10\%$ based on the accuracy of the photodiode. The blue arrow refers to the NIST evaluated experimental triphenylene ionization energy of 7.87 ± 0.02 eV.¹⁰

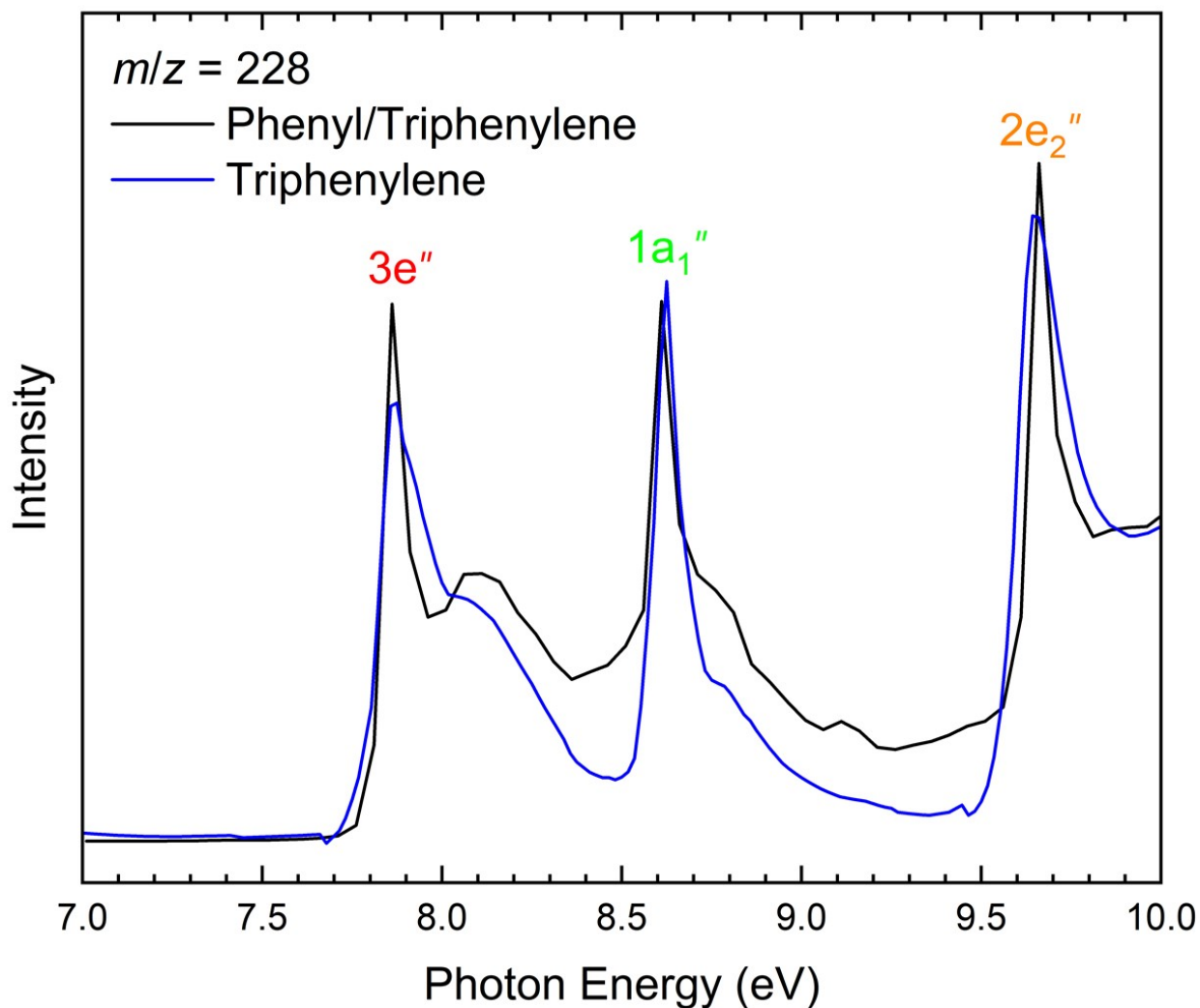


Fig. S2 (Black) mass-selective threshold photoelectron (ms-TPE) spectrum for the nitrosobenzene (C_6H_5NO) – triphenylene ($C_{18}H_{12}$) system at $m/z = 228$ ($C_{18}H_{12}$) (present work) and (blue) reference photoelectron spectrum of triphenylene digitized from Rademacher et al.¹¹ Molecular orbital assignments for electronic transitions to the ground, first excited, and second excited cation states of triphenylene from Deleuze¹² are shown in red, green, and orange, respectively.

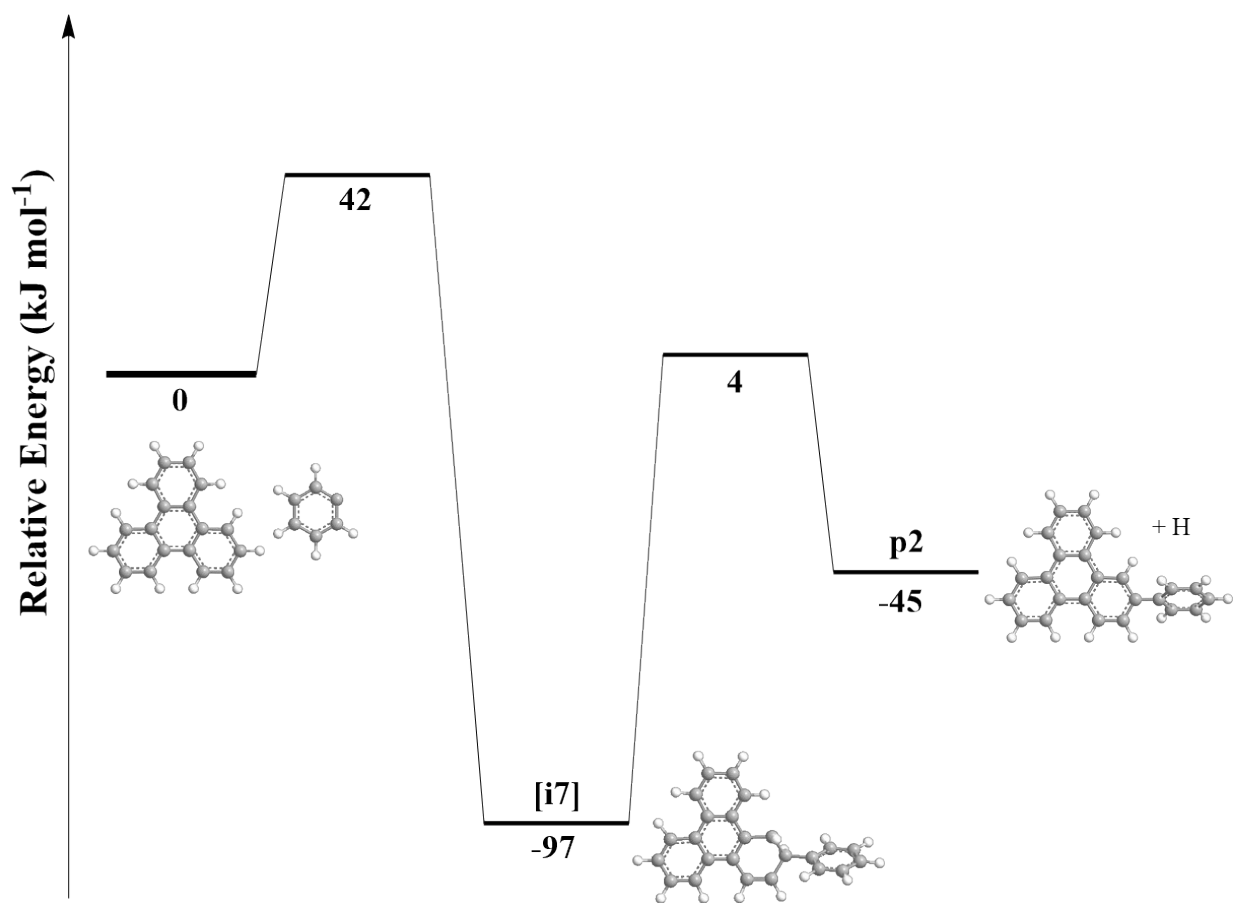


Fig. S3 Potential energy surface (PES) for the phenyl $[\text{C}_6\text{H}_5]^\bullet$ reaction with triphenylene ($\text{C}_{18}\text{H}_{12}$) calculated at the CCSD(T)/cc-pVDZ//B3LYP/cc-pVTZ level of theory leading to 2-phenyltriphenylene ($\text{C}_{24}\text{H}_{16}$).

Movies S1 and S2 “Butterfly” animation of vibrational modes ν_1 and ν_5 at 7.16 and 119.65 cm^{-1} , respectively.



mode1.mp4



mode5.mp4

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