Formation of Polycyclic Aromatic Hydrocarbons from Bimolecular Reactions of Phenyl Radicals at High Temperatures

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The supporting information contains figures S1-S11.

**Figure S1:** In a control experiment without pyrolysis and in the absence of FEL radiation trace amounts of aniline from the heated diazobenzene sample were identified by its REMPI spectrum, using a ps laser system. Aniline was identified by comparison with the spectra given in Ref 1 and 2.
Figure S2: IR/UV-spectrum of the peak at m/z = 230 (top trace) and computed IR spectra for the terphenyl isomers (lower traces). The best fit to the experimental spectrum shows the dominant contribution of the para isomer (second trace).
**Figure S3:** IR/UV-spectra of the mass peak at m/z = 152 recorded at 255 nm (top trace), 270 nm (second trace) and 285 nm (third trace) UV radiation. The two bands around 1500 and 1600 cm\(^{-1}\) are probably due to dissociative photoionization of biphenyl associated with H\(_2\) loss. The characteristic peak around 1210 cm\(^{-1}\) does not appear in the computed IR spectra of biphenylene (fourth trace), acenaphthylene (fifth trace) and cyclopenta[a]indene (lowest trace), which are possible candidates for m/z = 152. In turn peaks computed with high intensity do not appear in the experimental spectrum. Thus there is no evidence for formation of any of these species.
Figure S4: As visible in the center trace, small amounts of oxygen present in the pyrolysis lead to the formation of phenol (m/z = 94) from phenyl radical. The top trace shows, that the signal at m/z=66 is due to dissociative photoionisation of phenol.
Figure S5: The pyrolysis product m/z = 170 is identified as p-hydroxybiphenyl, which is formed in the presence of trace amounts of oxygen in the pyrolysis.
Figure S6: The IR/UV-spectrum of the peak at $m/z = 104$ (upper trace) was identified as styrene by its computed IR spectrum (lower trace).
Figure S7: The IR/UV-spectrum of the peak at m/z = 228 is rather noisy, but shows only a single peak in the low-wavenumber region at around 740 cm⁻¹. Ruling out 1-phenylethynyl naphthalene and chrysene by their experimental spectra, we assign this mass to triphenylene due to its high symmetry. Note that the IR/UV spectrum recorded at 255 nm shows a signal gain rather than a depletion.
Figure S8: The IR/UV-spectrum of the peak at m/z = 117 (upper trace) was assigned to indole by its computed IR spectrum (lower trace).

Figure S9: The IR/UV-spectrum of the peak at m/z = 169 (upper trace) was assigned to diphenylamine by its computed IR spectrum (lower trace).
Figure S10: The IR/UV-spectrum of the peak at m/z = 243 (upper trace) was assigned to 9-phenylcarbazole by its computed IR spectrum (lower trace).

Figure S11: The IR/UV-spectrum of the peak at m/z = 245 (upper trace) was assigned to triphenylamine by its computed IR spectrum (lower trace).
References