Supplementary Information

1,8-Bis(phenylethynyl)anthracene – gas and solid phase structures

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Computational methods

Quantum chemical calculations were performed with the GAUSSIAN 03,[S1] 09 program packages.[S2] Molecular force field calculations were carried out for all functionals and structural models to ensure that stationary points represent a minimum. Molecular dynamics calculations of the 1,8-BPEA were performed utilizing the *CP2K* code.[S3] The Quickstep method for density functional calculations using a mixed Gaussian and plane waves approach was applied.[S4] To model an isolated molecule using this periodic code a single molecule was simulated in a cubic supercell with the size of 17 Å. The BLYP (Becke-Lee-Yang-Parr) exchange-correlation functional and corresponding DZVP basis sets were used.

The equilibrium geometry of 1,8-BPEA was optimized, starting from the geometry calculated at the CAM-B3LYP/cc-pVTZ level of theory, and this structure together with force field was then used to determine the vibrational corrections using molecular dynamics simulations. The simulations were performed in the canonical (NVT) ensemble using a chain of five Nose-Hoover thermostats with time constant of 4 fs to regulate the simulation temperature at 498 K, approximately the temperature of the GED experiment. The simulations were run with a time step of 0.5 fs and lasted for 25 ps. The technique for calculating vibrational corrections using molecular dynamics data is described in ref. S5.

In addition, the geometry of 1-(phenylethynyl)anthracene, abbreviated 1-PEA was optimized under C_s symmetry [with torsion angle $\tau(C_{Ph}CCC_{Ant})$ = 0° for model A and $\tau(C_{Ph}CCC_{Ant})$ = 90° for model B, Fig. 6 (Paper)] utilizing LC-BLYP/cc-pVTZ and CAM-B3LYP/cc-pVTZ theoretical approximations.

A natural bond orbital analysis (NBO)[S6] for the 1,8-bis(phenylethynyl)anthracene and 1-(phenylethynyl)anthracene molecules was performed at CAM-B3LYP/cc-pVTZ level of theory.

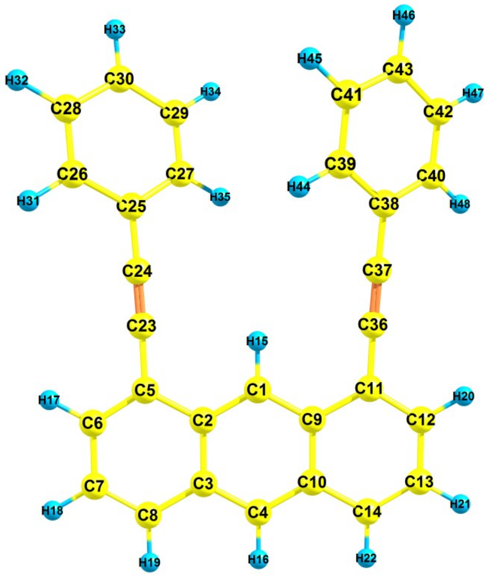
The molecular structure of the 1,8-BPEA was optimised and the force fields calculated under C_{2v} symmetry for models 1 and 3, C_s for models 2 and 5, C_2 for model 4. Models 1 and 3 were found to be saddle points of 2nd order, model 5 one of 1st order while the model 4 was found to be a minimum in all QC calculations. Model 2 corresponds to a saddle point of 1st order at or a minimum the LC-BLYP/cc-pVTZ level of theory. Therefore this model was also examined in GED structural analysis together with model 4. The relative energies of the models are presented in the Table 1 (Paper).

Table S1 Structural parameters of 1,8-BPEA determined by quantum chemical calculations

	LC-BLYP/cc-pVTZ	**LC-wPBE/cc-pVTZ**	**M06/cc-pVTZ**
Bond lengths			
r[C(1)–C(2)]	1.379	1.386	1.387
r[C(1)–C(9)]	1.379	1.386	1.387
r[C(1)–C(15)]	1.080	1.082	1.083
r[C(2)–C(3)]	1.414	1.420	1.428
r[C(2)–C(5)]	1.434	1.439	1.437
r[C(3)–C(4)]	1.379	1.386	1.390
r[C(3)–C(8)]	1.420	1.425	1.419
r[C(4)–C(10)]	1.379	1.386	1.390
r[C(4)–C(16)]	1.083	1.084	1.085
r[C(5)–C(6)]	1.351	1.358	1.369
r[C(5)–C(23)]	1.425	1.430	1.418
r[C(6)–C(7)]	1.413	1.417	1.410
r[C(6)–C(17)]	1.080	1.082	1.082
r[C(7)–C(8)]	1.341	1.349	1.359
r[C(7)–C(18)]	1.081	1.083	1.082
r[C(8)–C(19)]	1.082	1.084	1.084
r[C(9)–C(10)]	1.414	1.420	1.428
r[C(9)–C(11)]	1.434	1.439	1.437
r[C(10)–C(14)]	1.420	1.425	1.419
r[C(11)–C(12)]	1.351	1.358	1.369

r[C(11)–C(36)]	1.425	1.430	1.418
r[C(12)–C(13)]	1.413	1.417	1.410
r[C(12)–C(20)]	1.080	1.082	1.082
r[C(13)–C(14)]	1.341	1.349	1.359
r[C(13)–C(21)]	1.081	1.083	1.082
r[C(14)–C(22)]	1.082	1.084	1.084
r[C(23)–C(24)]	1.190	1.198	1.205
r[C(24)–C(25)]	1.426	1.432	1.420
r[C(25)–C(26)]	1.384	1.391	1.395
r[C(25)–C(27)]	1.384	1.390	1.397
r[C(26)–C(28)]	1.373	1.379	1.382
r[C(26)–C(31)]	1.080	1.082	1.082
r[C(27)–C(29)]	1.374	1.380	1.380
r[C(27)–C(35)]	1.080	1.082	1.084
r[C(28)–C(30)]	1.377	1.383	1.386
r[C(28)–C(32)]	1.081	1.083	1.082
r[C(29)–C(30)]	1.376	1.383	1.386
r[C(29)–C(34)]	1.081	1.083	1.082
r[C(30)–C(33)]	1.081	1.083	1.082
r[C(36)–C(37)]	1.190	1.198	1.205
r[C(37)–C(38)]	1.426	1.432	1.420
r[C(38)–C(39)]	1.384	1.390	1.397
r[C(38)–C(40)]	1.384	1.391	1.395
r[C(39)–C(41)]	1.374	1.380	1.380
r[C(39)–C(44)]	1.080	1.082	1.084
r[C(40)–C(42)]	1.373	1.379	1.382
r[C(40)–C(48)]	1.080	1.082	1.082
r[C(41)–C(43)]	1.376	1.383	1.386
r[C(41)–C(45)]	1.081	1.083	1.082
r[C(42)–C(43)]	1.377	1.383	1.386
r[C(42)–C(47)]	1.081	1.083	1.082
r[C(43)–C(46)]	1.081	1.083	1.082
Angles			
∠[C(2)–C(1)–C(9)]	121.5	121.4	121.8
∠[C(2)–C(1)–C(15)]	119.3	119.3	119.1
∠[C(1)–C(2)–C(3)]	119.3	119.3	119.2
∠[C(1)–C(2)–C(5)]	122.3	122.3	121.8
∠[C(9)–C(1)–C(15)]	119.3	119.3	119.1
∠[C(1)–C(9)–C(10)]	119.3	119.3	119.2
∠[C(1)–C(9)–C(11)]	122.3	122.3	121.8
∠[C(3)–C(2)–C(5)]	118.4	118.4	118.9
∠[C(2)–C(3)–C(4)]	119.1	119.1	118.9
∠[C(2)–C(3)–C(8)]	119.3	119.4	119.0
∠[C(2)–C(5)–C(6)]	119.9	119.9	119.6
∠[C(2)–C(5)–C(23)]	120.2	120.3	118.7
∠[C(4)–C(3)–C(8)]	121.5	121.5	122.1
∠[C(3)–C(4)–C(10)]	121.7	121.7	121.9
∠[C(3)–C(4)–C(16)]	119.2	119.2	119.1
∠[C(3)–C(8)–C(7)]	120.7	120.7	120.7
∠[C(3)–C(8)–C(19)]	118.4	118.5	118.5
∠[C(10)–C(4)–C(16)]	119.2	119.2	119.1
∠[C(4)–C(10)–C(9)]	119.1	119.1	118.9
∠[C(4)–C(10)–C(14)]	121.5	121.5	122.1
∠[C(6)–C(5)–C(23)]	119.9	119.7	121.7
∠[C(5)–C(6)–C(7)]	121.2	121.2	121.1
∠[C(5)–C(6)–C(17)]	119.2	119.2	119.1
∠[C(5)-C(23)-C(24)]	178.8	178.3	174.9
∠[C(7)-C(6)-C(17)]	119.6	119.6	119.9
∠[C(6)-C(7)-C(8)]	120.4	120.4	120.7
∠[C(6)–C(C7)–C(C18)]	119.1	119.1	119.1
∠[C(8)–C(7)–C(18)]	120.5	120.5	120.2
∠[C(7)–C(8)–C(19)]	120.8	120.8	120.8
∠[C(10)–C(9)–C(11)]	118.4	118.4	118.9
∠[C(9)–C(10)–C(14)]	119.3	119.4	119.0
∠[C(9)–C(11)–C(12)]	119.9	119.9	119.6
∠[C(9)–C(11)–C(36)]	120.2	120.3	118.7
∠[C(10)–C(14)–C(13)]	120.7	120.7	120.7
∠[C(10)–C(14)–C(22)]	118.4	118.5	118.5
∠[C(12)–C(11)–C(36)]	119.9	119.7	121.7
∠[C(11)–C(12)–C(13)]	121.2	121.2	121.1

∠[C(11)–C(12)–C(20)]	119.2	119.2	119.1
∠[C(11)–C(36)–C(37)]	178.8	178.3	174.9
∠[C(13)–C(12)–C(20)]	119.6	119.6	119.9
∠[C(12)–C(13)–C(14)]	120.4	120.4	120.7
∠[C(12)–C(13)–C(21)]	119.1	119.1	119.1
∠[C(14)–C(13)–C(21)]	120.5	120.5	120.2
∠[C(13)–C(14)–C(22)]	120.8	120.8	120.8
∠[C(23)–C(24)–C(25)]	179.5	179.3	176.8
∠[C(24)–C(25)–C(26)]	120.3	120.3	121.6
∠[C(24)–C(25)–C(27)]	120.4	120.5	119.4
∠[C(26)–C(25)–C(27)]	119.2	119.3	119.0
∠[C(25)–C(26)–C(28)]	120.3	120.2	120.2
∠[C(25)–C(26)–C(31)]	119.2	119.2	119.1
∠[C(25)–C(27)–C(29)]	120.3	120.2	120.4
∠[C(25)–C(27)–C(35)]	119.4	119.4	118.9
∠[C(28)–C(26)–C(31)]	120.5	120.5	120.7
∠[C(26)–C(28)–C(30)]	120.2	120.2	120.3
∠[C(26)–C(28)–C(32)]	119.7	119.7	119.7
∠[C(29)–C(27)–C(35)]	120.3	120.4	120.7
∠[C(27)–C(29)–C(30)]	120.2	120.2	120.2
∠[C(27)–C(29)–C(34)]	119.5	119.6	119.7
∠[C(30)–C(28)–C(32)]	120.1	120.1	120.0
∠[C(28)–C(30)–C(29)]	119.8	119.8	119.9
∠[C(28)–C(30)–C(33)]	120.1	120.1	120.1
∠[C(30)–C(29)–C(34)]	120.3	120.2	120.2
∠[C(29)–C(30)–C(33)]	120.1	120.1	120.1
∠[C(36)–C(37)–C(38)]	179.5	179.3	176.8
∠[C(37)–C(38)–C(39)]	120.4	120.5	119.4
∠[C(37)–C(38)–C(40)]	120.3	120.3	121.6
∠[C(39)–C(38)–C(40)]	119.2	119.3	119.0
∠[C(38)–C(39)–C(41)]	120.3	120.2	120.4
∠[C(38)–C(39)–C(44)]	119.4	119.4	118.9
∠[C(38)–C(40)–C(42)]	120.3	120.2	120.2
∠[C(38)–C(40)–C(48)]	119.2	119.2	119.1
∠[C(41)–C(39)–C(44)]	120.3	120.4	120.7
∠[C(39)–C(41)–C(43)]	120.2	120.2	120.2
∠[C(39)–C(41)–C(45)]	119.5	119.6	119.7
∠[C(42)–C(40)–C(48)]	120.5	120.5	120.7
∠[C(40)–C(42)–C(43)]	120.2	120.2	120.3
∠[C(40)–C(42)–C(47)]	119.7	119.7	119.7
∠[C(43)–C(41)–C(45)]	120.3	120.2	120.2
∠[C(41)–C(43)–C(42)]	119.8	119.8	119.9
∠[C(41)–C(43)–C(46)]	120.1	120.1	120.1
∠[C(43)–C(42)–C(47)]	120.1	120.1	120.0
∠[C(42)–C(43)–C(46)]	120.1	120.1	120.1



Structural analysis of gas phase electron diffraction data

Structural analysis of the GED data was carried out for the molecular models 2 and 4 of C_s and C_2 symmetry, respectively (Fig. 1, Paper). Fifteen independent parameters were chosen to describe both models. The set of independent parameters includes five bond lengths {r[C(10)–C(10a)], r[C(1)–C(11)], r[C(11)–C(12)], r[C(13)–C(18)], r[C(9)–H], six valence angles {∠[C(4a)–C(10)–C(10a)], ∠[C(9a)–C(4a)–C(4)], ∠[C(9a)–C(1)–C(11)], ∠[C(12)–C(11)–C(1)], ∠[C(12)–C(13)–C(18)], ∠[H–C(10)–C(10a)]} and three torsion angles {τ[C(18)–C(13)–C(12)–C(2)], τ[C(12)–C(11)–C(1)–C(9a)], τ[C(13)–C(12)–C(11)–C(1)]}; the dihedral angles τ[C(12)–C(11)–C(1)–C(9a)], τ[C(13)–C(12)–C(11)–C(1)] were fixed in the least-squares analysis at calculated values.

As far as the C–C bond lengths (1.36–1.45 Å) of 1,8-BPEA fall under the same peak of its radial distribution curve these distances cannot be resolved accurately. To weaken the high correlation between structural parameters, the differences between the bond lengths [all Δ(C–C) in the ring system, differences between the exocyclic distances Δ[C(1)–C(11)]−[C(12)–C(13)], Δ(C–H)] and also between the valence angles [Δ(∠CCC) in the ring system, Δ(∠CCH)] were taken from the results of the B3LYP/cc-pVTZ quantum-chemical calculations and were fixed in the analysis by the least-squares method. Starting values for independent parameters were taken from the above mentioned DFT computation. Dependent parameters were determined in terms of the geometrically consistent $r_\mathrm{e}$structure. The amplitudes were refined in groups corresponding to the different peaks on the radial distribution curve. Least-square analysis of the molecular intensity function, $sM(s)$ was performed by the modified KCED-35 program, which is similar to the algorithm described in ref. S7. Figs. 3 and 4 (Paper) display the plots of the $sM(s)$ (molecular intensity curve) and $f(r)$ (radial distribution curve) experimental and theoretical (model) functions. Refined geometrical and vibrational parameters for model 4 are listed in Table S2.

Table S2 Selected structural parameters of the 1,8-BPEA molecule determined by quantum-chemical calculations (single molecule), X-ray diffraction (XRD, single crystal) and GED (gas phase) experiments

	DFT/cc-pVTZ			XRD[b,c]		GED[c]					
	B3LYP	CAM-B3LYP	B3LYP-D3	minimum	maximum	r_e	r_g	$r_a - r_e$	l_{exp}	l_{calc}[g]	l_{calc}[h]
Bond lengths											
r[C(10)–C(4a)][d]	1.394	1.388	1.394	1.390(2)	1.396(2)	1.393(6)	1.398(6)	0.00373	0.046(2)	0.034	0.047
r[C(4a)–C(9a)]	1.438	1.428	1.438	1.430(2)	1.436(2)	1.437(6)	1.444(6)	0.00503	0.048(2)	0.036	0.049
r[C(9a)–C(9)]	1.395	1.389	1.393	1.389(2)	1.396(2)	1.393(6)	1.401(6)	0.00637	0.045(2)	0.033	0.047
r[C(4a)–C(4)]	1.423	1.423	1.424	1.421(2)	1.428(2)	1.422(6)	1.429(6)	0.00465	0.048(2)	0.036	0.048
r[C(4)–C(3)]	1.364	1.354	1.365	1.357(2)	1.359(2)	1.363(6)	1.368(6)	0.00407	0.043(2)	0.031	0.044
r[C(3)–C(2)]	1.412	1.413	1.413	1.410(2)	1.414(2)	1.411(6)	1.419(6)	0.00643	0.047(2)	0.035	0.048
r[C(1)–C(2)]	1.379	1.366	1.378	1.369(2)	1.375(2)	1.378(6)	1.385(6)	0.00579	0.045(2)	0.033	0.044
r[C(1)–C(9a)]	1.444	1.440	1.444	1.439(2)	1.445(2)	1.443(6)	1.452(6)	0.00674	0.050(2)	0.039	0.048
r[C(1)–C(11)][d]	1.419	1.424	1.418	1.426(2)	1.432(2)	1.422(7)	1.431(7)	0.00767	0.049(2)	0.037	
r[C(12)–C(13)]	1.422	1.426	1.420	1.428(2)	1.432(2)	1.424(7)	1.434(7)	0.00764	0.050(2)	0.038	
r[C(13)–C(14)]	1.403	1.395	1.403	1.386(2)	1.400(2)	1.411(6)	1.417(6)	0.00428	0.048(2)	0.036	
r[C(13)–C(18)][d]	1.404	1.395	1.404	1.386(2)	1.400(2)	1.411(6)	1.418(6)	0.00554	0.049(2)	0.037	
r[C(18)–C(17)]	1.386	1.381	1.386	1.379(2)	1.382(2)	1.393(6)	1.400(6)	0.00531	0.045(2)	0.033	
r[C(14)–C(15)]	1.387	1.382	1.386	1.379(2)	1.382(2)	1.394(6)	1.400(6)	0.00481	0.045(2)	0.033	
r[C(15)–C(16)]	1.391	1.385	1.391	1.367(2)	1.387(2)	1.398(6)	1.405(6)	0.00488	0.046(2)	0.034	
r[C(16)–C(17)]	1.391	1.386	1.392	1.367(2)	1.387(2)	1.399(6)	1.405(6)	0.00472	0.046(2)	0.034	
r[C(11)–C(12)][d]	1.209	1.200	1.208	1.201(2)	1.203(2)	1.205(8)	1.212(8)	0.00519	0.035(2)	0.023	
r[C(9)–H][d]	1.080	1.080	1.080	–	–	1.085(5)	1.096(5)	0.00602	0.069(7)	0.037	
r[C–C$_{av}$(Ant)][e]	1.410	1.403	1.406	1.403(2)	1.403(2)	1.409(6)					
r[C–C$_{av}$(Ph)][f]	1.394	1.387	1.394	1.380(2)	1.388(2)	1.401(6)					
Angles											
∠[C(8a)–C(9)–C(9a)]	121.9	121.7	121.8	121.4(1)	121.6(1)	120.4(54)					
∠[C(9a)–C(1)–C(2)]	119.5	119.7	119.5	119.4(1)	120.1(1)	117.7(30)					
∠[C(4a)–C(4)–C(3)]	120.7	120.7	120.7	120.3(1)	121.0(1)	120.4(4)					
∠[C(18)–C(13)–C(14)]	118.7	119.0	118.9	118.4(1)	119.3(1)	118.9(26)					
∠[C(15)–C(16)–C(17)]	119.7	119.8	119.8	119.4(1)	120.2(1)	119.9(27)					
∠[C(4a)–C(10)–C(10a)][d]	122.0	121.9	122.0	121.5(1)	122.0(1)	121.8(7)					
∠[C(9a)–C(4a)–C(4)][d]	119.4	119.4	119.2	119.4(1)	119.5(1)	119.2(4)					
∠[C(9a)–C(1)–C(11)][d]	121.1	120.7	120.1	118.6(1)	122.1(1)	120.2(29)					
∠[C(12)–C(13)–C(18)][d]	120.5	120.4	120.8	119.7(1)	121.5(1)	120.4(13)					
∠[C(1)–C(11)–C(12)]	177.5	178.1	178.2	173.1(1)	179.2(1)	179.8(33)					
∠[C(11)–C(12)–C(13)]	178.9	179.2	179.3	175.1(1)	179.1(1)	178.9(33)					
τ [C(18)–C(13)–C(12)–C(2)][d]	22.7	25.4	25.1	7.1(1)	37.6(1)	24.4(180)					

[a] Bond lengths are given in Å, angles in degrees. See Fig. 4 (Paper) for atom numbering.

[b] Only the non-disordered molecules (molecules 1–3) are taken into account.

[c] Experimental errors are given as 1σ for XRD and as $\sigma = [(0.002r)^2+(2.5\sigma\mathrm{LS})^2]^{1/2}$ for distances and $\sigma = 3\sigma\mathrm{LS}$ for vibrational amplitudes and angles for GED.

[d] Independent parameters.

[e] Average C–C distances in the anthracene fragment (XRD: range).

[f] Average C–C distances in the phenyl rings (XRD: range).

[g] Vibrational amplitudes calculated from MD.[S5,S8]

[h] Vibrational amplitudes for the anthracene were estimated using the program SHRINK.[S9]

Table S3 Lengths of linear chain for 1,8-BPEA, 1-PEA, DPE molecules

	$C_{Ant/Ph}$–C≡	**–C≡C–**	**–C≡C_{Ph}**	**$C_{Ant/Ph}$–C_{Ph}**
1,8-BPEA, model 1	1.424	1.201	1.425	4.050
1,8-BPEA, model 3	1.427	1.200	1.429	4.056
1,8-BPEA, model 4	1.424	1.200	1.426	4.050
1-PEA, model A	1.423	1.201	1.425	4.049
1-PEA, model B	1.427	1.200	1.429	4.056
Ph-C≡C-Ph, coplanar	1.425	1.200	1.425	4.050

Table S4 Conditions of the combined gas electron diffraction / mass spectrometry (GED/MS) experiment

Nozzle-to-plate distance *L*, mm	**338 (L_2)**	**598 (L_1)**
Electron beam current [μA]	1.75	0.90
Ionization voltage [V]	50	50
Temperature of effusion cell [K]	496(8)	499(5)
Wavelength of electrons λ [Å]	0.04004(5)	0.04038(3)
Exposition time [s]	100	94
Residual gas pressure “diffraction chamber/ MS-block” [Torr]	$2.0 \cdot 10^{-6}$	$2.3 \cdot 10^{-6}$
Number of films	5	5
s_{min}–s_{max}; Δs [Å^{-1}]	2.6–29.6; 0.1	1.3–16.7; 0.1

Table S5 Mass spectrometry data of 1,8-BPEA (ion intensities below 2% are omitted)

Ion	***m/z***	**Relative abundance [%]**	
		L_1 = 598 mm	**L_2 = 338 mm**
$[C_{30}H_{18}]^+$	378	100	100
$[M–Ph]^+$	301	7	6
$[C_{15}H_9]^+$	189	18	17
$[C_{15}H_5]^+$	185	15	14
$[C_{14}H_8]^+$	176	6	6
$[C_{14}H_6]^+$	173	5	5
$[C_{13}H_9]^+$	165	3	3
$[C_{13}H_6]^+$	160	2	2
$[C_{12}H_8]^+$	152	3	3

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