

Supporting Information for

Gas-phase equilibrium molecular structures and *ab initio* thermochemistry of anthracene and rubrene

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Table S1. Conditions of GED/MS experiments for anthracene

Nozzle-to-film distance, mm	338	598
Primary electron beam current, μA	1.72	0.86
Accelerating voltage, kV	90	88
Temperature of effusion cell, $^{\circ}\text{C}$	122(5)	123(5)
Wavelength of electrons, \AA	0.03926(4)	0.03979(3)
Average exposure time, s	83	67
Residual gas pressure, Torr		
• in diffraction chamber	$1.8 \cdot 10^{-6}$	$3.1 \cdot 10^{-6}$
• in mass-spectrometric block	$4.8 \cdot 10^{-7}$	$5 \cdot 10^{-7}$
Ionization voltage, V	50	50
Recorded films, substance/standard	6/2	6/2
s -range/ Δs , \AA^{-1}	3.1-30.2/0.1	1.3-16.9/0.1
Inflection points for background ^a	2	2
Experimental weighted R -factor, % ^b	4.99	2.65
Experimental R -factor, %	12.20	5.59

^a For reduced intensities of anthracene.

^b Calculated as $[\sum_i^N \sum_j^M \omega_j (s_j M_i(s_j) - s_j M_{\text{av}}(s_j))^2 / N \sum_j^M \omega_j (s_j M_{\text{av}}(s_j))^2]^{1/2} \times 100\%$, where $s_j M_i(s_j)$ is the experimental molecular intensity from set i in point s_j , $s_j M_{\text{av}}(s_j)$ is the average molecular intensity curve in the point s_j , ω_j is the weight of the averaged $sM(s)$ calculated from the respective standard deviation as $1/\sigma^2$, N is the number of data sets, M is the number of points in each set.

^c Calculated with all $\omega_j = 1$.

Table S2. Conditions of GED/MS experiments for rubrene

Nozzle-to-film distance, mm	338	598
Primary electron beam current, μA	1.71	0.44
Accelerating voltage, kV	74	73
Temperature of effusion cell, $^{\circ}\text{C}$	228(5)	225(5)
Wavelength of electrons, \AA	0.04364(4)	0.04380(3)
Average exposure time, s	140	61
Residual gas pressure, Torr		
• in diffraction chamber	$1.9 \cdot 10^{-6}$	$2.1 \cdot 10^{-6}$
• in mass-spectrometric block	$8.7 \cdot 10^{-7}$	$8.0 \cdot 10^{-7}$
Ionization voltage, V	50	50
Recorded films, substance/standard	6/2	6/2
s -range/ Δs , \AA^{-1}	3.0-27.1/0.1	1.2-15.4/0.1
Inflection points for background ^a	4	3
Experimental weighted R -factor, % ^b	5.35	3.17
Experimental R -factor, % ^c	10.14	4.26

^a For reduced intensities of rubrene.

^{b,c} See notes in Table S1.

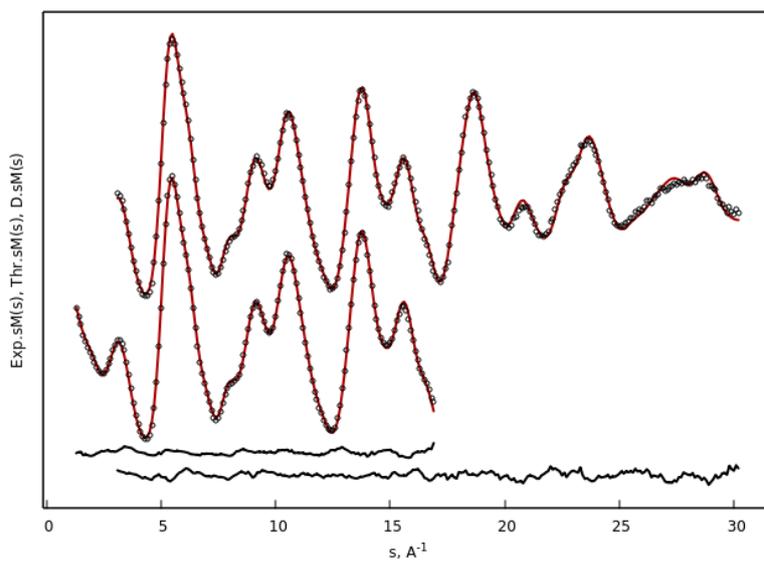


Figure S1. Experimental (dots) and corresponding model (lines) molecular intensity functions $sM(s)$ for anthracene.

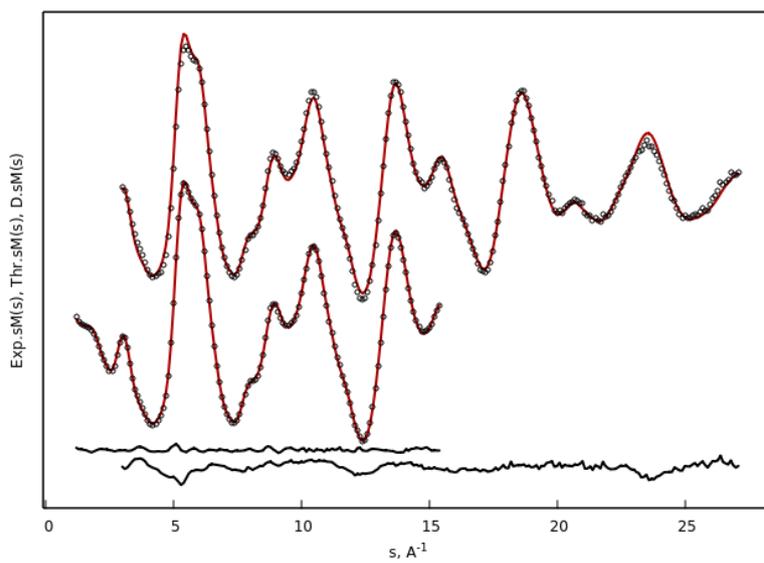


Figure S2. Experimental (dots) and corresponding model (lines) molecular intensity functions $sM(s)$ for rubrene.

Table S3. Mass spectra of anthracene vapor recorded simultaneously with electron diffraction measurements. ^a

Ion	m/e	$I, \%$	
		LD	SD
$[\text{C}_{14}\text{H}_{10}]^+$	178	100	100
$[\text{C}_{12}\text{H}_8]^+$	152	9	8
$[\text{C}_7\text{H}_5]^+$	89	29	24
$[\text{C}_6\text{H}_3]^+$	75	25	25
$[\text{C}_5\text{H}_3]^+$	63	8	8
$[\text{C}_4\text{H}_3]^+$	51	3	3

^a The following atomic weights (amu) were used in the interpretation of the mass spectra: C,12; H, 1; the ion intensities below 1% are omitted.

Table S4. Mass spectra of rubrene vapor recorded simultaneously with electron diffraction measurements. ^a

Ion	m/e	$I, \%$	
		LD	SD
$[\text{C}_{42}\text{H}_{28}]^+$	532	100	100
$[\text{C}_{36}\text{H}_{23}]^+$	455	36	35
$[\text{C}_{35}\text{H}_{19}]^+$	439	4	4
$[\text{C}_{34}\text{H}_{16}]^+$	424	3	3
$[\text{C}_{33}\text{H}_{16}]^+$	412	1	2
$[\text{C}_{30}\text{H}_{18}]^+$	378	45	44
$[\text{C}_{42}\text{H}_{28}]^{++}$	266	2	2
$[\text{C}_{36}\text{H}_{23}]^{++}$	228	10	10
$[\text{C}_{35}\text{H}_{19}]^{++}$	220	8	9
$[\text{C}_{34}\text{H}_{16}]^{++}$	212	5	5
$[\text{C}_{33}\text{H}_{13}]^{++}$	205	2	2
$[\text{C}_{30}\text{H}_{18}]^{++}$	189	14	14

^a The following atomic weights (amu) were used in the interpretation of the mass spectra: C,12; H, 1; the ion intensities below 1% are omitted.

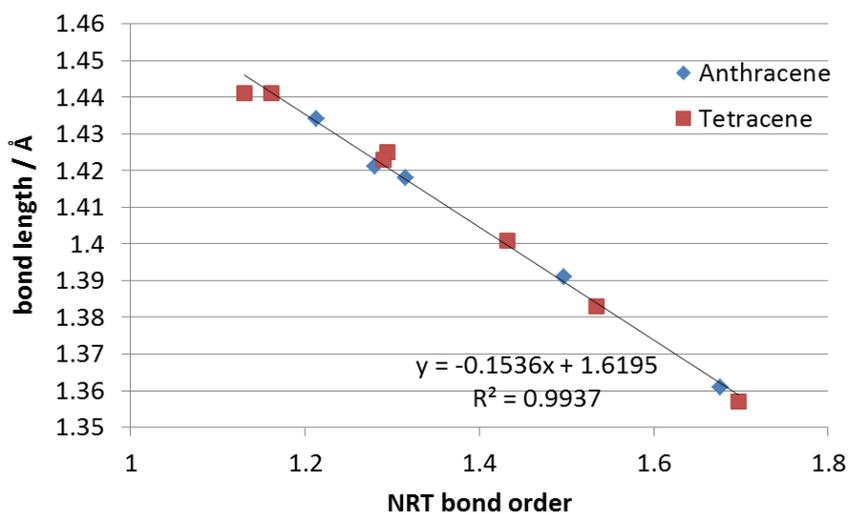


Figure S3. Correlation between NRT bond orders and corresponding bond lengths for the structures optimized at PBE0-D3(BJ)/def2-TZVP level of theory.

Table S5. Selected molecular parameters of tetracene and rubrene optimized at PBE0-D3(BJ)/def2-TZVP level of theory. ^a

Parameter	Tetracene	Rubrene
$r(\text{C4a-C5})$	1.383	1.394
$r(\text{C5-C5a})$	1.401	1.419
$\angle(\text{C4a-C5-C5a})$	121.8	120.0

^a Bond lengths are given in Å, bond angle in degrees.

Table S6. Reference gas-phase enthalpies of formation used in this work.

Molecule	$\Delta_f H_m^\circ$ (g, 298.15 K)
CH ₄ (methane)	-74.526±0.049 ^a
C ₂ H ₆ (ethane)	-84.04±0.13 ^a
C ₂ H ₄ (ethylene)	52.32±0.12 ^a
C ₆ H ₆ (benzene)	83.12±0.22 ^a
C ₈ H ₁₀ (ethylbenzene)	29.73±0.55 ^a
C ₈ H ₈ (phenylethene)	148.34±0.55 ^a
C ₄ H ₆ (1,3-butadiene)	110.90±0.33 ^a
C ₆ H ₁₂ (cyclohexane)	-122.94±0.30 ^a
C ₄ H ₈ (isobutene)	-17.01±0.39 ^a
C ₅ H ₁₂ (<i>neo</i> -pentane)	-167.39±0.39 ^a
C ₅ H ₆ (cyclopentadiene)	134.15±0.63 ^a
C ₄ H ₁₀ (<i>iso</i> -butane)	-134.62±0.30 ^a
C ₇ H ₈ (toluene)	50.11±0.33 ^a
C ₁₀ H ₈ (naphthalene)	149.0±0.4 ^{a,b}
C ₁₆ H ₁₀ (pyrene)	224.7±2.9 ^{a,b}

^a Retrieved from the ATcT database. ^b Obtained from the reaction-based Feller-Peterson-Dixon approach and the ATcT reference values, see Section 3.1 of ref. ¹

- 1 I. Minenkova, A. A. Otlyotov, L. Cavallo and Y. Minenkov, Gas-phase thermochemistry of polycyclic aromatic hydrocarbons: An approach integrating the quantum chemistry composite scheme and reaction generator, *Phys. Chem. Chem. Phys.*, 2022, **24**, 3163–3181.