Supporting Information for: Low-Lying $\pi\pi^*$ Excited States in Five-Membered Ring Heterocycles: A Continuing Challenge

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S-I. Additional computational details

Additional electronic structure calculations with ADC and TDDFT methods were performed with Q-CHEM 6.3.1[1]. Excited-state analysis was enabled by the `STATE_ANALYSIS TRUE` keyword. For tellurophene ground- and excited-state calculations, we used the Stuttgart–Köln pseudopotential[2]. Spin–orbit coupling was not treated for any of the considered compounds, although it may be important for systems containing heavy atoms; these effects are beyond the scope of this work.

The state-averaged complete active space self-consistent field (SA-CASSCF) and extended multi-state complete active space second-order perturbation theory (XMS-CASPT2) calculations were performed for singlet states, using an imaginary shift of 0.2 a.u. and the aug-cc-pVTZ basis set. Symmetry constraints were not applied. A minimal active space of 4 electrons in 4 π orbitals ($HOMO-1$, $HOMO$, $LUMO$, and $LUMO+1$, as shown in Figure 3 of the main text) was used to capture the main excited-state features, although larger active spaces may be required for quantitative predictions. For *cis*-butadiene, furan, pyrrole, and thiophene, three states were included in the state averaging (ground and two excited states). In the case of benzene, state averaging with six states was used to preserve orbital symmetry, as other choices led to orbital distortions. Multireference calculations were performed with the BAGEL 1.2.2 package[3].

Orbitals and structures were visualized using VMD 1.9.3[4].

S-II. Theory vs. experiment

Experimental peak maxima for furan, pyrrole, and thiophene A_1 and B_2 lowest $\pi\pi^*$ singlet states are listed in Table S1. Despite being common practice, band maxima should not be directly compared to vertical excitation energies provided by theory,[5] since vertical excitation energy is not an experimental observable. In practice, vertical excitation energies are typically blue-shifted with respect to the band maximum. For instance, in *trans*-butadiene, nearly exact vertical excitation energy was computed at the QMC-FCI level.[6] The vertical excitation energy of the B_u state ($HOMO \rightarrow LUMO$) appears shifted by as much as 0.4 eV from the experimental maximum. To make the comparison between experiment and theory feasible, different approaches have been proposed. "Experimental vertical excitation" energies can be obtained by back-correcting experimental 0-0 energies with theoretically estimated relaxation energy, solvent effects, and zero-point vibrational energy.[7] This requires optimization of excited states with an adequate level of theory. Such an approach was successfully applied to linear acenes, but it is not very convenient for the present set of molecules. In thiophene, B_2 is likely an unbound state, as suggested by spectroscopy[8] (structureless broad band) and nonadiabatic simulations[9], which identified barrierless non-radiative decay to the ground state via a conical intersection. For the A_1 state of thiophene, there is an ambiguity about the excited-state minimum structure when using different levels of theory.[9,10] The same is true for the B_2 state of pyrrole, which is planar when diffuse basis sets are employed and otherwise non-planar; this effect is due to large valence–Rydberg mixing.[11] The 0-0 experimental transitions are furthermore not available for the dark A_1 states of furan and pyrrole.

An alternative approach comprises computing a shift between the band maximum and the vertical excitation energy purely by theory, and "correcting" the experimental band maximum by adding the theoretical shift value. Crespo-Otero and Barbatti simulated absorption cross sections of furan by the nuclear ensemble apprach along with the ADC(2) electronic structure, and estimated a maximum-to-vertical shift of 0.15 eV for the B_2 state.[12] Barbatti

and Sen estimated the "experimental vertical excitation" of pyrrole B_2 as 6.12 eV, which is 0.17 eV higher than the experimental maximum estimated at 5.95 eV.[13] Unfortunately, shift values are not available for the dark A_1 states of pyrrole and furan – the absorption of very weak A_1 states is hidden behind the strong B_2.[14] Maximum-to-vertical shifts for thiophene can be deduced from the nuclear ensemble approach,[9] being approximately 0.2 eV for B_2 and 0.25 eV for A_1. Although experimental results for excited-state maxima are somewhat spread, by adding the maximum-to-vertical shifts we find solid agreement with CC3 and ADC(3) (Table S1) — the latter predicting slightly lower energies than CC3. Multireference results are also scattered, depending on the method, active space, basis set, and shift techniques employed. Since our excitation energies were computed using the same geometries as the CC3 values, the best strategy is presumably to compare the results with the theoretical best estimates from the CC3 method.

Table S1: Excitation energies (eV) from different levels of theory. The present ADC(3) excitation energies were obtained with the aug-cc-pVTZ basis set using the same geometries as CC3; oscillator strengths are given in parentheses.

	ADC(3)	CC3[a]	multireference	experimental
$^1B_2^+$ (furan)	6.15 (0.1663)	6.34	6.19[b]; 6.19[c]; 6.20[d]	6.04[j]; 6.01[k]; 6.06[l]
$^1A_1^-$ (furan)	6.48 (0.0004)	6.58	6.35[b]; 6.45[c]; 6.77[d]	-
$^1B_2^+$ (pyrrole)	6.11 (0.1710)	6.25	6.22[b]; 6.29[e]; 6.24[f]	5.95[m]; 5.89/5.98[l]
$^1A_1^-$ (pyrrole)	6.29 (0.0004)	6.32	6.23[b]; 6.18[e]; 6.01[f]	-
$^1B_2^+$ (thiophene)	5.79 (0.0845)	5.96	5.92[g]; 6.14[h]; 6.00[i]	5.64[n]; 5.70[k]; 5.93[l]
$^1A_1^-$ (thiophene)	5.61 (0.0768)	5.65	5.58[g]; 5.85[h]; 5.69[i]	5.26,[n] 5.33[k]; 5.48[l]

[a] CC3/aug-cc-pVTZ of Loos *et al.*[15]
[b] MS-CASPT2/aug-cc-pVTZ of Silva-Junior *et al.*[16]
[c] MS-CASPT2/6-311+G*+sp of Stenrup and Larson[17]
[d] NEVPT2/aug-cc-pVTZ of Loos *et al.*[15]
[e] XMS-CASPT2/ANO-L+ of Heindl and Gonzalez[18]
[f] CASPT2/aug-cc-pVDZ+ of Neville and Worth[19]
[g] CASPT2/6-31G* of Kölle *et al.*[20]
[h] MS-CASPT2/6-311G* of Stenrup[21]
[i] MRCI/QZVP by Palmer *et al.*[22]
[j] Vacuum ultraviolet spectrum of Palmer *et al.*[23]
[k] Ultraviolet spectra of Igarashi *et al.*[24] (assignment opposite for thiophene)
[l] Electron energy-loss spectra of Flicker *et al.*[25]
[m] Maximum value from Barbatti and Sen[13]
[n] Magnetic circular dichroism of Håkansson *et al.*[26]

S-III. Supporting data

Table S2: Vertical $\pi\pi^*$ excitation energies (eV) calculated using ADC methods with aug-cc-pVTZ, along with CC3 reference data; oscillator strengths given in parentheses.

Molecule	State	ADC(1)	ADC(2)	ADC(3)	CC3
	$^1B_2^+$	5.45	5.45	5.33 (0.2851)	5.55
	$^1A_1^-$	8.10*	7.59	5.50 (0.0018)	6.71
cis-butadiene	$^1A_1^+$	8.59	8.76*	8.34 (0.2776)	—
	$^3B_2^-$	2.35	3.15	2.80	—
	$^3A_1^-$	4.20	5.16	4.81	—
	$^1B_{1u}^+$	6.18	6.45	6.24 (0.0000)	6.44
	$^1B_{2u}^-$	6.02	5.27	5.00 (0.0000)	5.09
benzene	$^1E_{1u}$	7.66*	7.17	7.08 (0.6712)	—
	$^3B_{1u}^-$	3.41	4.37	3.94	4.18
	$^3B_{2u}^-$	4.90	5.07	4.59	4.86
	$^1B_2^+$	6.35	6.48	6.15 (0.1663)	6.34
	$^1A_1^-$	7.94	6.76	6.48 (0.0004)	6.58
furan	$^1A_1^+$	8.64*	8.29*	7.99 (0.3363)	—
	$^3B_2^-$	3.38	4.41	3.90	4.22
	$^3A_1^-$	4.91	5.59	5.22	5.48
	$^1B_2^+$	6.28*	6.36*	6.11* (0.1710)	6.25
	$^1A_1^-$	7.35	6.47	6.29 (0.0004)	6.32
pyrrole	$^1A_1^+$	8.19*	7.89*	7.52* (0.3550)	—
	$^3B_2^-$	3.79	4.70	4.25	4.53
	$^3A_1^-$	5.15	5.62	5.22	5.46

Molecule	State	ADC(1)	ADC(2)	ADC(3)	CC3
thiophene	$^1B_2^+$	6.03	6.07	5.78 (0.0845)	5.96
	$^1A_1^-$	6.62	5.70	5.60 (0.0768)	5.65
	$^1A_1^+$	8.23*	7.51*	7.16 (0.2731)	7.35
	$^3B_2^-$	3.19	4.11	3.64	3.94
	$^3A_1^-$	4.54	4.85	4.55	4.77
arsole	$^1A''$	4.98	4.99	4.76 (0.0369)	—
	$^1A'$	6.03	5.00	5.11 (0.0820)	—
	$^3A''$	2.36	3.22	2.82	—
	$^3A'$	4.09	4.38	4.27	—
phosphole	$^1A''$	5.02	5.04	4.78 (0.0406)	—
	$^1A'$	6.00	4.98	5.00 (0.1118)	—
	$^1A''$	2.40	3.27	2.87	—
	$^1A'$	3.97	4.18	3.99	—
selenophene	$^1B_2^+$	5.75	5.82	5.50 (0.0730)	—
	$^1A_1^-$	6.19	5.26	5.28 (0.1087)	—
	$^3B_2^-$	2.95	3.89	3.39	—
	$^3A_1^-$	4.29	4.47	4.28	—
tellurophene	$^1B_2^+$	5.40	5.49	5.19 (0.0442)	—
	$^1A_1^-$	5.54	4.54	4.68 (0.1344)	—
	$^3B_2^-$	2.73	3.66	3.18	—
	$^3A_1^-$	3.93	3.89	3.79	—

* Valence-Rydberg mixed states are identified based on NTOs and large electron size (see Table S4).

Table S3: Vertical $\pi\pi^*$ excitation energies (eV) calculated using TDDFT with aug-cc-pVTZ, along with CC3 reference data; TDA in parentheses.

Molecule	State	BLYP	B3LYP	CAM-B3LYP	CC3
	$^1B_2^+$	4.77 (5.16)	4.93 (5.30)	5.08 (5.42)	5.55
	$^1A_1^-$	6.16 (6.19)	6.74 (6.78)	7.38 (7.42)	6.71
cis-butadiene	$^1A_1^+$	7.89* (8.08*)	8.15* (8.39*)	8.39* (8.64*)	—
	$^3B_2^-$	2.69 (2.88)	2.51 (2.86)	2.36 (2.87)	—
	$^3A_1^-$	4.89 (5.05)	4.73 (4.98)	4.60 (4.91)	—
	$^1B_{1u}^+$	5.89 (6.13)	6.04 (6.26)	6.15 (6.37)	6.44
	$^1B_{2u}^-$	5.20 (5.22)	5.39 (5.42)	5.48 (5.53)	5.09
benzene	$^1E_{1u}$	6.75 (7.00*)	6.93 (7.28*)	7.04 (7.45*)	—
	$^3B_{1u}^-$	4.06 (4.25)	3.83 (4.19)	3.59 (4.14)	4.18
	$^3B_{2u}^-$	4.63 (4.67)	4.70 (4.76)	4.77 (4.83)	4.86
	$^1B_2^+$	5.81 (6.02*)	5.99 (6.24)	6.11 (6.38*)	6.34
	$^1A_1^-$	6.25 (6.30)	6.63 (6.68)	6.95 (7.01)	6.58
furan	$^1A_1^+$	7.69* (7.86*)	7.86* (8.20*)	8.08* (8.41*)	—
	$^3B_2^-$	3.95 (4.09)	3.78 (4.05)	3.65 (4.02)	4.22
	$^3A_1^-$	5.26 (5.36)	5.21 (5.36)	5.18 (5.34)	5.48
	$^1B_2^+$	5.64* (5.68*)	5.94* (6.01*)	6.14* (6.25*)	6.25
	$^1A_1^-$	6.06 (6.12)	6.39 (6.45)	6.65 (6.73)	6.32
pyrrole	$^1A_1^+$	7.21* (7.37*)	7.50* (7.72*)	7.72* (7.98*)	—
	$^3B_2^-$	4.26 (4.38)	4.13 (4.36)	4.00 (4.33)	4.53
	$^3A_1^-$	5.21 (5.27)	5.23 (5.33)	5.24 (5.36)	5.46

Molecule	State	BLYP	B3LYP	CAM-B3LYP	CC3
thiophene	$^1B_2^+$	5.51 (5.82)	5.64 (5.94)	5.74 (6.05)	5.96
	$^1A_1^-$	5.53 (5.64)	5.75 (5.86)	5.87 (6.00)	5.65
	$^1A_1^+$	6.87* (7.35*)	7.22* (7.69*)	7.47* (7.95*)	7.35
	$^3B_2^-$	3.69 (3.83)	3.53 (3.79)	3.39 (3.77)	3.94
	$^3A_1^-$	4.41 (4.45)	4.46 (4.54)	4.44 (4.56)	4.77
arsole	$^1A''$	4.33 (4.55)	4.50 (4.73)	4.67 (4.91)	—
	$^1A'$	4.52 (4.62)	4.81 (4.89)	5.06 (5.14)	—
	$^3A''$	2.78 (2.94)	2.61 (2.91)	2.47 (2.92)	—
	$^3A'$	3.78 (3.82)	3.95 (4.02)	4.06 (4.20)	—
phosphole	$^1A''$	4.38 (4.62)	4.55 (4.80)	4.70 (4.96)	—
	$^1A'$	4.69 (4.84)	4.92 (5.05)	5.09 (5.22)	—
	$^3A''$	2.85 (3.00)	2.68 (2.97)	2.54 (2.96)	—
	$^3A'$	3.64 (3.69)	3.75 (3.83)	3.81 (3.95)	—
selenophene	$^1B_2^+$	5.25 (5.56)	5.38 (5.67)	5.48 (5.77)	—
	$^1A_1^-$	5.18 (5.32)	5.36 (5.50)	5.46 (5.61)	—
	$^3B_2^-$	3.46 (3.60)	3.29 (3.56)	3.14 (3.53)	—
	$^3A_1^-$	4.07 (4.11)	4.13 (4.19)	4.12 (4.23)	—
tellurophene	$^1B_2^+$	4.93 (5.18)	5.06 (5.30)	5.17 (5.41)	
	$^1A_1^-$	4.54 (4.69)	4.69 (4.84)	4.80 (4.95)	
	$^3B_2^-$	3.25 (3.39)	3.07 (3.35)	2.90 (3.32)	—
	$^3A_1^-$	3.52 (3.55)	3.59 (3.65)	3.63 (3.73)	—

* Valence-Rydberg mixed states are identified based on NTOs and large electron size (see Table S4).

Table S4: Electron size values (in Å) for the $\pi\pi^*$ excited states from Tables S2 and S3; TDA in parentheses.

Molecule	State	ADC(1)	ADC(2)	ADC(3)	BLYP	B3LYP	CAM-B3LYP
	$^1B_2^+$	2.33	2.25	2.27	2.28 (2.47)	2.25 (2.39)	2.21 (2.34)
	$^1A_1^-$	4.13*	2.23	1.98	2.17 (2.19)	2.22 (2.26)	2.20 (2.31)
cis-butadiene	$^1A_1^+$	2.88	3.32*	2.45	3.57* (4.00*)	3.33* (3.74*)	3.33* (3.48*)
	$^3B_2^-$	1.88	1.91	1.91	1.93 (1.95)	1.89 (1.93)	1.87 (1.91)
	$^3A_1^-$	1.86	1.89	1.89	1.92 (1.94)	1.89 (1.91)	1.86 (1.89)
	$^1B_{1u}^+$	2.15	2.16	2.16	2.17 (2.24)	2.14 (2.20)	2.12 (2.16)
	$^1B_{2u}^-$	2.11	2.00	2.01	2.04 (2.05)	2.04 (2.04)	2.02 (2.02)
benzene	$^1E_{1u}$	3.39*	2.39	2.48	2.55 (3.34*)	2.42 (3.12*)	2.34 (2.93*)
	$^3B_{1u}^-$	1.90	1.91	1.91	1.92 (1.94)	1.89 (1.92)	1.87 (1.91)
	$^3B_{2u}^-$	1.99	1.98	1.97	1.97 (1.98)	1.96 (1.97)	1.95 (1.96)
	$^1B_2^+$	2.52	2.40	2.33	2.64 (3.07*)	2.43 (2.79)	2.29 (2.58)
	$^1A_1^-$	2.60	1.99	1.98	2.13 (2.14)	2.10 (2.12)	2.05 (2.08)
furan	$^1A_1^+$	3.11*	3.15*	2.77	3.42* (3.66*)	3.05* (3.39*)	3.39* (3.20*)
	$^3B_2^-$	1.74	1.77	1.75	1.76 (1.79)	1.73 (1.76)	1.71 (1.74)
	$^3A_1^-$	1.78	1.82	1.80	1.87 (1.88)	1.82 (1.84)	1.79 (1.81)
	$^1B_2^+$	3.39*	3.26*	3.07*	3.55* (3.68*)	3.33* (3.56*)	3.04* (3.38*)
	$^1A_1^-$	2.67	2.14	2.13	2.45 (2.50)	2.34 (2.38)	2.23 (2.27)
pyrrole	$^1A_1^+$	3.43*	3.31*	3.28*	3.38* (3.72*)	3.18* (3.58*)	3.32* (3.45*)
	$^3B_2^-$	1.80	1.84	1.82	1.85 (1.88)	1.80 (1.84)	1.77 (1.81)
	$^3A_1^-$	1.89	1.94	1.90	2.00 (2.02)	1.93 (1.95)	1.88 (1.90)

Molecule	State	ADC(1)	ADC(2)	ADC(3)	BLYP	B3LYP	CAM-B3LYP
thiophene	$^1B_2^+$	2.09	2.09	2.07	2.11 (2.19)	2.08 (2.14)	2.04 (2.07)
	$^1A_1^-$	2.16	2.02	2.04	2.09 (2.12)	2.07 (2.10)	2.04 (2.10)
	$^1A_1^+$	3.56*	2.92*	2.55	3.22* (3.45*)	3.06* (3.21*)	2.94* (3.14*)
	$^3B_2^-$	1.84	1.87	1.86	1.88 (1.90)	1.85 (1.88)	1.83 (1.86)
	$^3A_1^-$	1.90	1.92	1.92	1.92 (1.92)	1.91 (1.92)	1.89 (1.90)
arsole	$^1A''$	2.14	2.16	2.16	2.24 (2.40)	2.17 (2.26)	2.12 (2.19)
	$^1A'$	2.25	2.08	2.12	2.10 (2.12)	2.10 (2.11)	2.09 (2.10)
	$^3A''$	1.87	1.92	1.91	1.96 (1.98)	1.91 (1.94)	1.88 (1.92)
	$^3A'$	1.93	2.06	2.04	2.05 (2.05)	2.04 (2.04)	2.02 (2.04)
phosphole	$^1A''$	2.10	2.11	2.11	2.18 (2.32)	2.12 (2.19)	2.08 (2.13)
	$^1A'$	2.19	2.06	2.09	2.12 (2.16)	2.10 (2.13)	2.08 (2.10)
	$^3A''$	1.87	1.91	1.90	1.95 (1.97)	1.91 (1.94)	1.88 (1.92)
	$^3A'$	1.95	2.01	2.01	2.01 (2.01)	2.00 (2.00)	1.98 (1.99)
selenophene	$^1B_2^+$	2.13	2.14	2.12	2.18 (2.26)	2.13 (2.19)	2.09 (2.14)
	$^1A_1^-$	2.25	2.09	2.11	2.17 (2.22)	2.14 (2.18)	2.11 (2.14)
	$^3B_2^-$	1.89	1.92	1.91	1.94 (1.96)	1.91 (1.93)	1.88 (1.91)
	$^3A_1^-$	1.97	1.99	1.99	1.99 (1.99)	1.97 (1.98)	1.96 (1.97)
tellurophene	$^1B_2^+$	2.21	2.24	2.22	2.29 (2.36)	2.24 (2.29)	2.18 (2.23)
	$^1A_1^-$	2.39	2.18	2.24	2.27 (2.32)	2.24 (2.28)	2.22 (2.25)
	$^3B_2^-$	1.95	2.01	1.99	2.04 (2.06)	2.00 (2.03)	1.96 (2.00)
	$^3A_1^-$	2.10	2.11	2.12	2.10 (2.11)	2.09 (2.10)	2.08 (2.09)

* Valence-Rydberg mixed states are identified based on NTOs and large electron size.

Table S5: Diffuseness ($\langle X^2 \rangle$, in a.u.) for the low-lying $\pi\pi^*$-like $^1B_2$ state of pyrrole, along with the energy gap (ΔE, in eV) to the lowest Rydberg-like $^1B_2$ state.

Level	cc-pVTZ		aug-cc-pVTZ		d-aug-cc-pVTZ	
	$\langle X^2 \rangle$	ΔE	$\langle X^2 \rangle$	ΔE	$\langle X^2 \rangle$	ΔE
ADC(1)	26.19	2.64	44.34	0.61	69.31	0.60
ADC(2)	25.73	1.54	41.32	0.56	65.24	0.54
ADC(3)	25.91	1.90	38.51	0.58	56.88	0.47

Table S6: ADC(3)/aug-cc-pVTZ configuration weights (%) for the low-lying B_2/L_a singlet and triplet state, based on NTO analysis.

Molecule	State	Ω	H→L	H−1→L+1	Other Singles	Non-singles
cis-butadiene	$^1B_2^+$	88.44	85.64	0.33	2.47	11.56
	$^3B_2^-$	89.92	82.93	4.90	2.09	10.08
benzene	$^1B_{1u}^+$	86.96	42.48	42.48	2.00	13.04
	$^3B_{1u}^-$	91.27	42.69	42.69	5.89	8.73
furan	$^1B_2^+$	87.88	84.64	0.89	2.35	12.12
	$^3B_2^-$	89.24	82.98	4.45	1.81	10.76
pyrrole	$^1B_2^+$	86.78	84.27	1.26	1.25	13.22
	$^3B_2^-$	89.01	82.68	4.64	1.70	10.99
thiophene	$^1B_2^+$	85.28	79.58	1.65	4.04	14.72
	$^3B_2^-$	88.20	82.39	3.90	1.91	11.80
arsole	$^1A''$	84.90	79.18	3.46	2.26	15.10
	$^3A''$	88.49	82.66	3.91	1.92	11.51
phosphole	$^1A''$	83.76	79.00	2.62	2.14	16.24
	$^3A''$	88.22	82.67	3.68	1.87	11.78
selenophene	$^1B_2^+$	84.62	78.38	1.31	4.93	15.38
	$^3B_2^-$	87.95	82.52	3.47	1.96	12.05
tellurophene	$^1B_2^+$	83.60	74.84	0.85	7.91	16.40
	$^3B_2^-$	87.67	82.17	3.42	2.08	12.33

Table S7: ADC(3)/aug-cc-pVTZ configuration weights (%) for the low-lying A_1/L_b singlet and triplet states, based on NTO analysis. For selected compounds, values for the high-lying *plus* singlet state were also reported.

Molecule	State	Ω	H−1→L	H→L+1	Other Singles	Non-singles
cis-butadiene	$^1A_1^-$	23.22	15.22	7.89	0.11	76.78
	$^1A_1^+$	76.77	62.27	10.78	3.72	23.23
	$^3A_1^-$	91.80	57.25	32.86	1.69	8.20
benzene	$^1B_{2u}^-$	80.11	39.76	39.76	0.59	19.89
	$^1E_{1u}(^1B_{2u}^+)$	87.35	46.08	36.95	4.32	12.65
	$^3B_{2u}^-$	82.47	41.10	40.91	0.46	17.53
furan	$^1A_1^-$	72.17	36.43	35.24	0.50	27.83
	$^1A_1^+$	77.78	37.19	36.44	4.15	22.22
	$^3A_1^-$	88.42	44.48	42.77	1.17	11.58
pyrrole	$^1A_1^-$	79.58	44.02	34.90	0.66	20.42
	$^1A_1^+$	85.17	37.33	45.38	2.46	14.83
	$^3A_1^-$	86.64	49.88	35.88	0.88	13.36
thiophene	$^1A_1^-$	80.99	64.96	14.07	1.96	19.01
	$^1A_1^+$	63.28	20.81	37.16	5.31	36.72
	$^3A_1^-$	86.32	76.71	8.65	0.97	13.68
arsole	$^1A'$	82.90	78.24	3.17	1.49	17.10
	$^3A'$	87.39	76.27	8.89	2.23	12.61
phosphole	$^1A'$	82.51	76.13	4.23	2.15	17.49
	$^3A'$	87.00	80.10	5.28	1.62	13.00
selenophene	$^1A_1^-$	81.86	69.92	9.30	2.64	18.14
	$^3A_1^-$	86.24	80.37	4.95	0.92	13.76
tellurophene	$^1A_1^-$	82.53	74.23	4.26	4.04	17.47
	$^3A_1^-$	85.82	83.05	1.84	0.93	14.18

Table S8: Vertical $\pi\pi^*$ excitation energies (eV) calculated using TDDFT with aug-cc-pVTZ, employing density functionals other than those reported in Table S3 and the main text; TDA results in parentheses.

Molecule	State	PBE	PBE0	ωB97X-D	M06-2X	CC3
	$^1B_2^+$	5.93 (6.16)	6.11 (6.38)	6.15 (6.44)	6.18 (6.44)	6.34
	$^1A_1^-$	6.33 (6.39)	6.79 (6.84)	6.96 (7.03)	7.05 (7.12)	6.58
furan	$^1A_1^+$	7.72 (8.04)	8.03 (8.36)	8.06 (8.48)	8.03 (8.36)	—
	$^3B_2^-$	3.95 (4.11)	3.66 (4.00)	3.82 (4.13)	4.22 (4.40)	4.22
	$^3A_1^-$	5.28 (5.38)	5.16 (5.35)	5.31 (5.46)	5.56 (5.65)	5.48
	$^1B_2^+$	5.81 (5.87)	6.11 (6.20)	6.21 (6.34)	6.17 (6.25)	6.25
	$^1A_1^-$	6.16 (6.22)	6.55 (6.61)	6.68 (6.76)	6.75 (6.82)	6.32
pyrrole	$^1A_1^+$	7.36 (7.55)	7.66 (7.91)	7.66 (8.07)	7.67 (7.92)	—
	$^3B_2^-$	4.27 (4.40)	4.03 (4.33)	4.17 (4.45)	4.57 (4.73)	4.53
	$^3A_1^-$	5.24 (5.31)	5.23 (5.35)	5.35 (5.45)	5.55 (5.61)	5.46
	$^1B_2^+$	5.59 (5.91)	5.75 (5.97)	5.77 (6.09)	5.86 (6.17)	5.96
	$^1A_1^-$	5.60 (5.71)	5.85 (6.04)	5.89 (6.03)	5.91 (6.05)	5.65
thiophene	$^1A_1^+$	7.01 (7.49)	7.39 (7.87)	7.53 (8.07)	7.70 (7.91)	7.35
	$^3B_2^-$	3.69 (3.84)	3.42 (3.76)	3.54 (3.86)	3.98 (4.15)	3.94
	$^3A_1^-$	4.42 (4.47)	4.44 (4.55)	4.54 (4.64)	4.64 (4.72)	4.77

Table S9: Vertical $\pi\pi^*$ excitation energies (eV) from SA-CASSCF(4,4)/aug-cc-pVTZ and XMS-CASPT2(4,4)/aug-cc-pVTZ; oscillator strengths in parentheses. In the case of benzene, we also report a high-lying doubly excited A_{1g} state.

Molecule	State	CASSCF	CASPT2	CC3
cis-butadiene	$^1B_2^+$	7.26	5.07 (0.2959)	5.55
	$^1A_1^-$	6.48	6.35 (0.0043)	6.71
benzene	$^1B_{1u}^+$	7.57	5.85 (0.0000)	6.44
	$^1B_{2u}^-$	6.82	4.50 (0.0000)	5.09
	$^1A_{1g}^-$	12.10	9.44 (0.0000)	—
furan	$^1B_2^+$	8.12	6.02 (0.2142)	6.34
	$^1A_1^-$	6.75	6.43 (0.0000)	6.58
pyrrole	$^1B_2^+$	7.48	6.00 (0.2909)	6.25
	$^1A_1^-$	6.56	6.15 (0.0005)	6.32
thiophene	$^1B_2^+$	7.81	5.28 (0.1301)	5.96
	$^1A_1^-$	6.29	5.80 (0.0208)	5.65

Table S10: Main SA-CASSCF(4,4) CI configuration weights (%) of low-lying singlet B_2/L_a state.

Molecule	$H \rightarrow L$	$H-1 \rightarrow L+1$
cis-butadiene	95.34	0.19
benzene	49.97	49.97
furan	96.33	0.95
pyrrole	96.41	1.52
thiophene	96.24	1.37

Table S11: Main SA-CASSCF(4,4) CI configuration weights (%) of low-lying singlet A_1/L_b state. Note that the L_b state of benzene does not contain the $H, H \rightarrow L, L$ configuration, which is a component of the high-lying A_{1g}^- state (see Table S9).

Molecule	$H-1 \rightarrow L$	$H \rightarrow L+1$	$H, H \rightarrow L, L$
cis-Butadiene	25.86	12.28	40.34
Benzene	49.65	49.65	-
Furan	39.05	30.25	12.18
Pyrrole	51.32	27.75	3.64
Thiophene	47.72	25.83	8.24

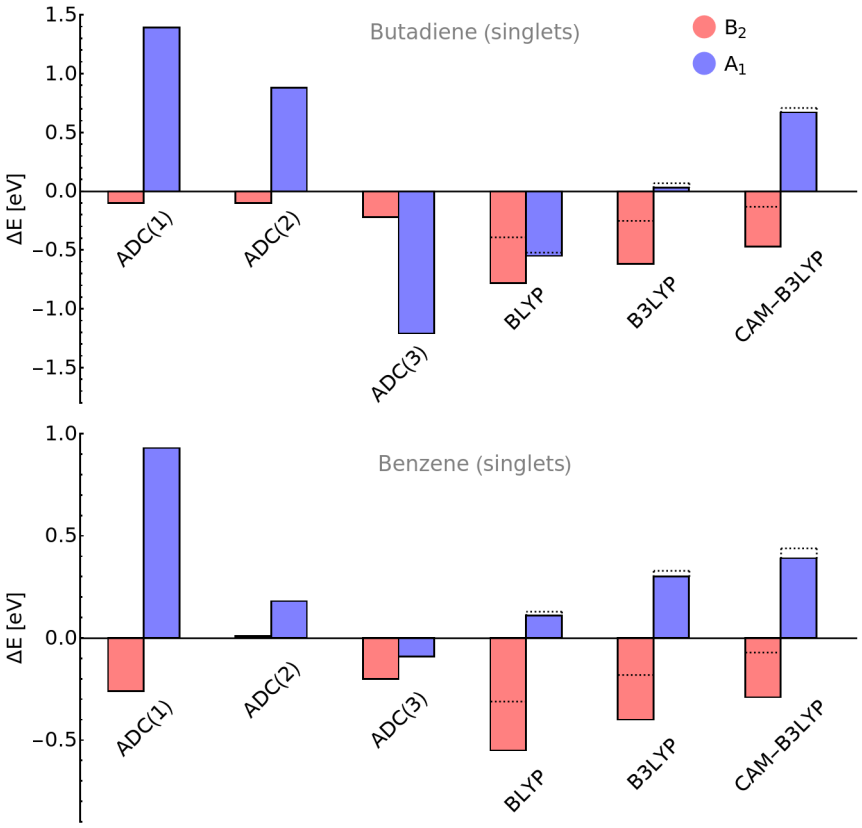

Figure S1: Deviation of excitation energies for the low-lying singlet excited states, A_1/L_b and B_2/L_a, from the CC3 reference. Results for *cis*-butadiene/benzene. Bars with dotted lines correspond to the TDA. All data were obtained with the aug-cc-pVTZ basis set.

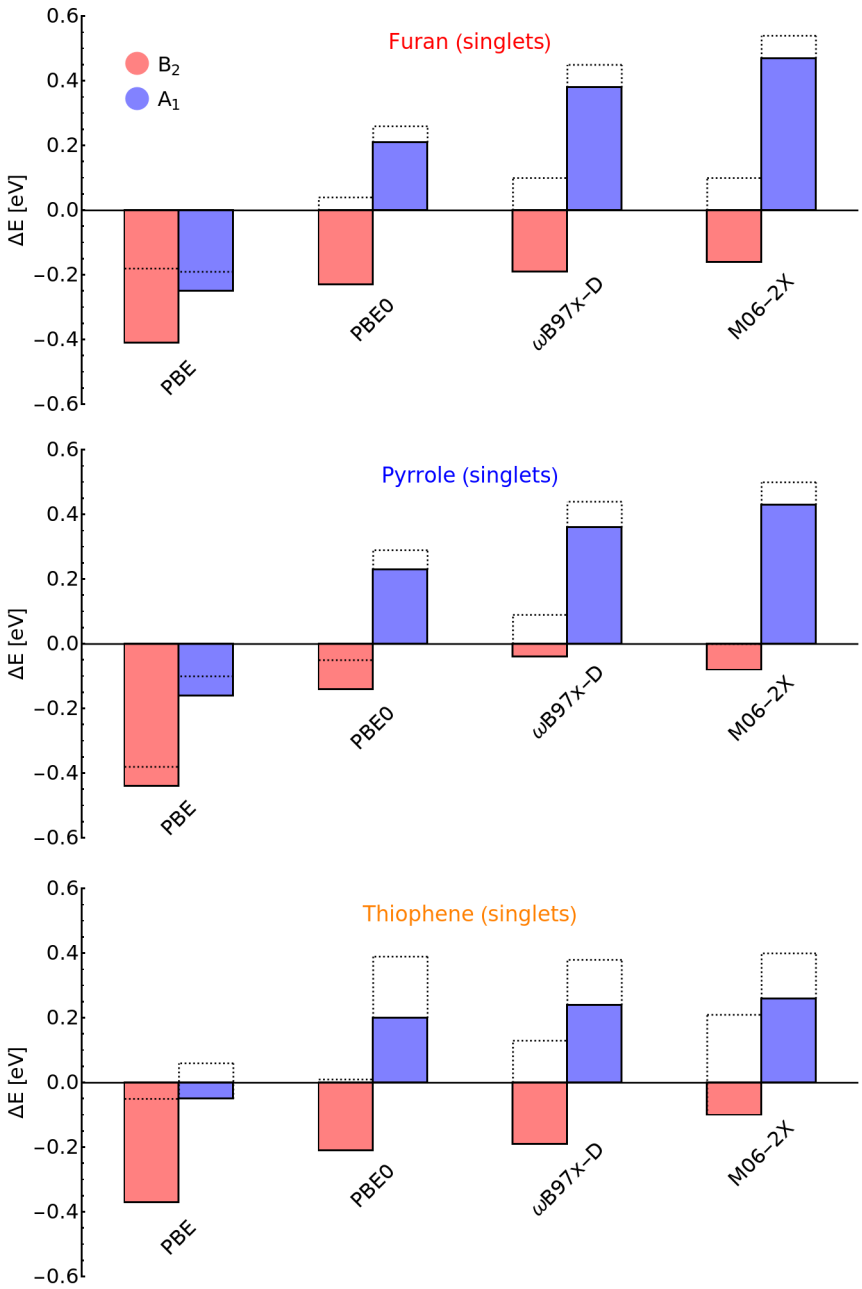

Figure S2: Deviation of excitation energies of the low-lying singlet excited states, A_1 and B_2, from the CC3 reference. TDDFT results for heterocycles using other density functionals. Bars with dotted lines correspond to the TDA. All data were obtained with the aug-cc-pVTZ basis set.

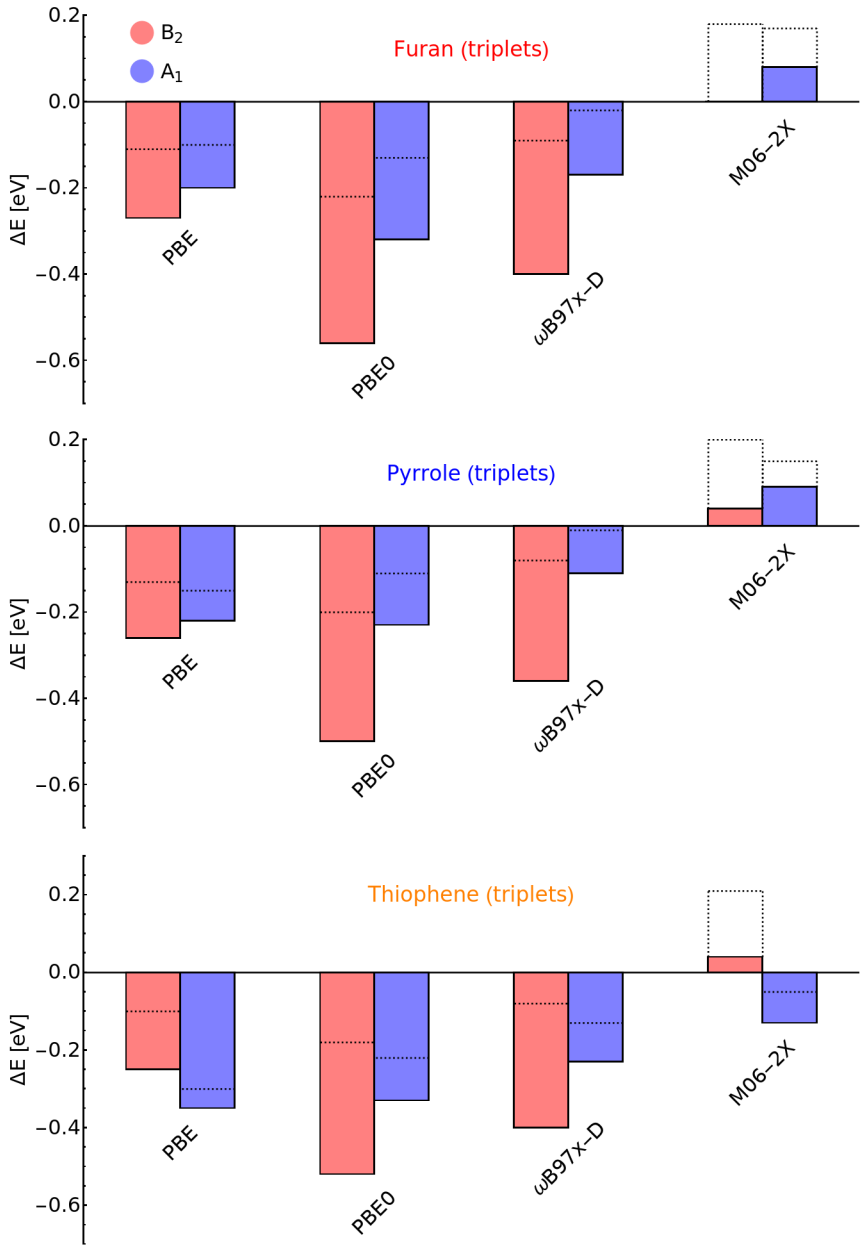

Figure S3: Deviation of excitation energies of the low-lying triplet excited states, A_1 and B_2, from the CC3 reference. TDDFT results for heterocycles using other density functionals. Bars with dotted lines correspond to the TDA. All data were obtained with the aug-cc-pVTZ basis set.

S-IV. Cartesian coordinates

All geometries are in standard XYZ format, in Angstrom units.

Cis-butadiene

```
C     0.0000000   0.6330921  -0.7335985
H     0.0000000   1.6085666  -1.2058788
C     0.0000000  -0.4475613  -1.5269261
H     0.0000000  -0.3410515  -2.6018885
H     0.0000000  -1.4530423  -1.1272432
C     0.0000000   0.6330921   0.7335985
H     0.0000000   1.6085666   1.2058788
C     0.0000000  -0.4475613   1.5269261
H     0.0000000  -0.3410515   2.6018885
H     0.0000000  -1.4530423   1.1272432
```

Arsole

```
C     0.3241420  -0.0802858   1.3147425
C    -0.8962365  -0.1544713   0.7257013
C    -0.8962365  -0.1544713  -0.7257013
C     0.3241420  -0.0802858  -1.3147425
H     0.4818199  -0.0821022   2.3832635
H    -1.8192495  -0.2003464   1.2906942
H    -1.8192495  -0.2003464  -1.2906942
H     0.4818199  -0.0821022  -2.3832635
As    1.7091454  -0.2080790   0.0000000
H     2.1099039   1.2424907   0.0000000
```

Phosphole

C	0.3299043	0.0568746	1.2819599
C	-0.9129232	0.1152856	0.7226881
C	-0.9129232	0.1152856	-0.7226881
C	0.3299043	0.0568746	-1.2819599
H	0.5296320	0.0666931	2.3430968
H	-1.8263184	0.1586045	1.3019556
H	-1.8263184	0.1586045	-1.3019556
H	0.5296320	0.0666931	-2.3430968
P	1.5753507	0.2403703	0.0000000
H	2.1840593	-1.0352867	0.0000000

Selenophene

C	0.0000000	0.5562622	-1.2794794
C	0.0000000	-0.6943497	-0.7080962
C	0.0000000	-0.6943497	0.7080962
C	0.0000000	0.5562622	1.2794794
H	0.0000000	0.7959502	-2.3305807
H	0.0000000	-1.5976961	-1.3016656
H	0.0000000	-1.5976961	1.3016656
H	0.0000000	0.7959502	2.3305807
Se	0.0000000	1.8796662	0.0000000

Tellurophene

C	0.0000000	0.5431378	-1.3428158
C	0.0000000	-0.6758203	-0.7097998

C	0.0000000	-0.6758203	0.7097998
C	0.0000000	0.5431378	1.3428158
H	0.0000000	0.6949395	-2.4112082
H	0.0000000	-1.5975550	-1.2780611
H	0.0000000	-1.5975550	1.2780611
H	0.0000000	0.6949395	2.4112082
Te	0.0000000	2.0706167	0.0000000

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