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A Mountaineering Strategy to Excited States: Highly Accurate Energies and Benchmarks for Medium Sized Molecules

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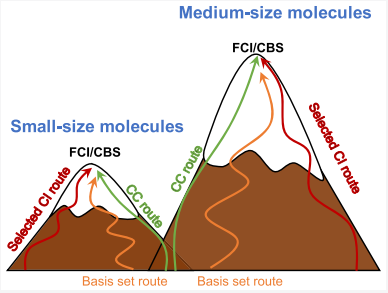
ABSTRACT: Following our previous work focusing on compounds containing up to 3 non-hydrogen atoms [*J. Chem. Theory Comput.* **2018**, *14*, 4360−4379], we present here highly accurate vertical transition energies obtained for 27 molecules encompassing 4, 5, and 6 non-hydrogen atoms: acetone, acrolein, benzene, butadiene, cyanoacetylene, cyanoformaldehyde, cyanogen, cyclopentadiene, cyclopropenone, cyclopropenethione, diacetylene, furan, glyoxal, imidazole, isobutene, methylenecyclopropene, propynal, pyrazine, pyridazine, pyridine, pyrimidine, pyrrole, tetrazine, thioacetone, thiophene, thiopropynal, and triazine. To obtain these energies, we use equation-of-motion/linear-response coupled cluster theory up to the highest technically possible excitation order for these systems (CC3, EOM-CCSDT, and EOM-CCSDTQ) and selected configuration interaction (SCI) calculations (with tens of millions of determinants in the reference space), as well as the multiconfigurational *n*-electron valence state perturbation theory (NEVPT2) method. All these approaches are applied in combination with diffuse-containing atomic basis sets. For all transitions, we report at least CC3/*aug*-cc-pVQZ vertical excitation energies as well as CC3/*aug*-cc-pVTZ oscillator strengths for each dipole-allowed transition. We show that CC3 almost systematically delivers transition energies in agreement with higher-level methods with a typical deviation of ±0.04 eV, except for transitions with a dominant double excitation character where the error is much larger. The present contribution gathers a large, diverse, and accurate set of more than 200 highly accurate transition energies for states of various natures (valence, Rydberg, singlet, triplet, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, ...). We use this series of theoretical best estimates to benchmark a series of popular methods for excited state calculations: CIS(D), ADC(2), CC2, STEOM-CCSD, EOM-CCSD, CCSDR(3), CCSDT-3, CC3, and NEVPT2. The results of these benchmarks are compared to the available literature data.



1. INTRODUCTION

Accurately describing transition energies between the electronic ground state (GS) and excited states (ESs) remains an important challenge in quantum chemistry. When dealing with large compounds in complex environments, one is typically limited to the use of time-dependent density-functional theory (TD-DFT),[1−3] a successful yet far from flawless approach. In particular, to perform TD-DFT calculations, one must choose an "appropriate" exchange-correlation functional, which is difficult yet primordial as the impact of the exchange-correlation functional is exacerbated within TD-DFT as compared to DFT.[4] Such a selection can, of course, rely on the intrinsic features of the various exchange-correlation functional families; e.g., it is well-known that range-separated hybrids provide a more physically sound description of long-range charge-transfer transitions than semilocal exchange-correlation functionals in the adiabatic TD-DFT framework.[5,6] However, to obtain a quantitative assessment of the accuracy that can be expected from TD-DFT calculations, benchmarks cannot be avoided. This is why so many assessments of TD-DFT performance for various ES properties are available.[4]

While several of these benchmarks rely on experimental data as reference (typically band shapes[7−14] or 0-0 energies[8,15−22]), theoretical best estimates (TBEs) based on state-of-the-art computational methods[23−28] are advantageous as they allow comparisons on a perfectly equal footing (same geometry, vertical transitions, no environmental effects, etc.). In such a case, the challenge is in fact to obtain accurate TBEs, as top-notch theoretical models generally come with a dreadful scaling with system size and, in addition, typically require large atomic basis sets to deliver transition energies close to the complete basis set (CBS) limit.[29]

More than 20 years ago, Serrano-Andrès, Roos, and collaborators compiled an impressive series of reference transition energies for typical conjugated organic molecules (butadiene, furan, pyrrole, tetrazine, etc.).[30−38] To this end, they relied on experimental GS geometries and the complete-active-

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space second-order perturbation theory (CASPT2) approach with the largest active spaces and basis sets one could dream of at the time. These CASPT2 values were later used to assess the performance of TD-DFT combined with various exchange-correlation functionals[39,40] and remained for a long time the best theoretical references available on the market. However, beyond comparisons with experiments, which are always challenging when computing vertical transition energies,[14] there was no approach available at that time to ascertain the accuracy of these transition energies. Nowadays, it is of common knowledge that CASPT2 has the tendency of underestimating vertical excitation energies in organic molecules when the IPEA shift is not included. It is also known that the use of a standard value of 0.25 au for this IPEA shift may lead to overestimations of the transition energies, making the use of this shift questionable.[41]

A decade ago, Thiel and co-workers defined TBEs for 104 singlet and 63 triplet valence ESs in 28 small and medium conjugated CNOH organic molecules.[23,25,26] These TBEs were computed on MP2/6-31G(d) structures with several levels of theory, notably CASPT2 and various coupled cluster (CC) variants (CC2, CCSD, and CC3). Interestingly, while the default theoretical protocol used by Thiel and co-workers to define their first series of TBEs was CASPT2,[23] the vast majority of their most recent TBEs (the so-called "TBE-2" in ref 26) were determined at the CC3 level of theory with the *aug*-cc-pVTZ (aVTZ) basis set, often using a basis set extrapolation technique. More specifically, CC3/TZVP values were corrected for basis set incompleteness errors by the difference between, e.g., the CC2/aVTZ and CC2/TZVP results.[25,26] Many works have exploited Thiel's TBEs for assessing lower-order methods,[24,42−68] highlighting further their value for the electronic structure community. In contrast, the number of extensions/improvements of this original set remains quite limited. For example, Kánnár and Szalay computed, in 2014, CCSDT/TZVP reference energies for 17 singlet states of six molecules.[69] Three years later, the same authors reported 46 CCSDT/aVTZ transition energies in small compounds containing two or three non-hydrogen atoms (ethylene, acetylene, formaldehyde, formaldimine, and formamide).[70]

Following the same philosophy, two years ago, we reported a set of 106 transition energies for which it was technically possible to reach the full configuration interaction (FCI) limit by performing high-order CC (up to CCSDTQP) and selected CI (SCI) calculations on CC3/aVTZ GS structures.[28] We exploited these TBEs to benchmark many ES methods.[28] Among our conclusions, we found that CCSDTQ yields near-FCI quality excitation energies, whereas we could not detect any significant differences between CC3 and CCSDT transition energies, both being very accurate with mean absolute errors (MAEs) as small as 0.03 eV compared to FCI.

Although these conclusions agree well with earlier studies,[69−71] they obviously only hold for single excitations, i.e., transitions with $\%T_1$, the single-excitation character in CC3 calculations, in the 80−100% range. Therefore, we also recently proposed a set of 20 TBEs for transitions exhibiting a significant double-excitation character (i.e., with $\%T_1$ typically below 80%).[72] Unsurprisingly, our results clearly evidenced that the error in the CC methods is intimately related to the $\%T_1$ value. For example, for the ES with a significant yet not dominant double excitation character [such as the infamous A_g ES of butadiene ($\%T_1$ = 75%)] CC methods including triples deliver rather accurate estimates (MAE of 0.11 eV with CC3 and 0.06 eV with CCSDT), surprisingly outperforming second-order multireference schemes such as CASPT2 or the generally robust *n*-electron valence state perturbation theory (NEVPT2). In contrast, for ESs with a dominant double excitation character, e.g., the low-lying $(n, n) \rightarrow (\pi^*, \pi^*)$ excitation in nitrosomethane ($\%T_1$ = 2%), single-reference methods (not including quadruples) have been found to be unsuitable with MAEs of 0.86 and 0.42 eV for CC3 and CCSDT, respectively. In this case, multiconfigurational methods are in practice required to obtain accurate results.[72]

A clear limit of our 2018 work[28] was the size of the compounds put together in our set. These were limited to 1−3 non-hydrogen atoms, hence introducing a potential "chemical" bias. Therefore, we have decided, in the present contribution, to consider larger molecules with organic compounds encompassing 4, 5, and 6 non-hydrogen atoms. For such systems, performing CCSDTQ calculations with large one-electron basis sets is elusive. Moreover, the convergence of the SCI energy with respect to the number of determinants is obviously slower for these larger compounds; hence, extrapolating to the FCI limit with an error of ∼0.01 eV is rarely achievable in practice. Consequently, the "brute-force" determination of FCI/CBS estimates, as in our earlier work,[28] is definitely out of reach here. Anticipating this problem, we have recently investigated bootstrap CBS extrapolation techniques.[28,72] In particular, we have demonstrated that, following an ONIOM-like scheme,[73] one can very accurately estimate such a limit by correcting high-level values obtained in a small basis by the difference between CC3 results obtained in a larger basis and those in the same small basis.[28] We globally follow such a strategy here. In addition, we also perform NEVPT2 calculations in an effort to check the consistency of our estimates. This is particularly critical for ES with intermediate $\%T_1$ values. Using this protocol, we define a set of more than 200 *aug*-cc-pVTZ reference transition energies, most being within ±0.03 eV of the FCI limit. These reference energies are obtained on CC3/aVTZ geometries, and additional basis set corrections (up to quadruple-ζ at least) are also provided for CC3. Together with the results obtained in our two earlier works,[28,72] the present TBE will hopefully contribute to climbing a rung higher on the ES accuracy ladder.

2. COMPUTATIONAL DETAILS

Unless otherwise stated, all transition energies are computed in the frozen-core approximation (with a large core for the sulfur atoms). Pople's 6-31+G(d) and Dunning's *aug*-cc-pVXZ (X = D, T, Q, and 5) atomic basis sets are systematically employed in our excited-state calculations. In the following, we employ the aVXZ shorthand notations for these diffuse-containing basis sets. We note that an alternative family of more compact diffuse basis sets (such as *jun*-cc-pVTZ) have been proposed by Truhlar and co-workers.[74] Such variants could be better suited to reach CBS-quality transition energies at a smaller computational cost. As we intend to provide benchmark values here, we nevertheless stick to the original Dunning's bases, which are directly available in almost any quantum chemistry codes. Various statistical quantities are reported in the remainder of this paper: the mean signed error (MSE), mean absolute error (MAE), root-mean-square error (RMSE), the standard deviation of the errors (SDE), and the maximum positive [Max(+)] and negative [Max(−)] errors. Here, we globally follow the same procedure as in ref 28, so that we only briefly outline the various theoretical methods that we have employed in the subsections below.

2.1. Geometries. The molecules considered herein are displayed in Scheme 1. Consistently with our previous work,[28]

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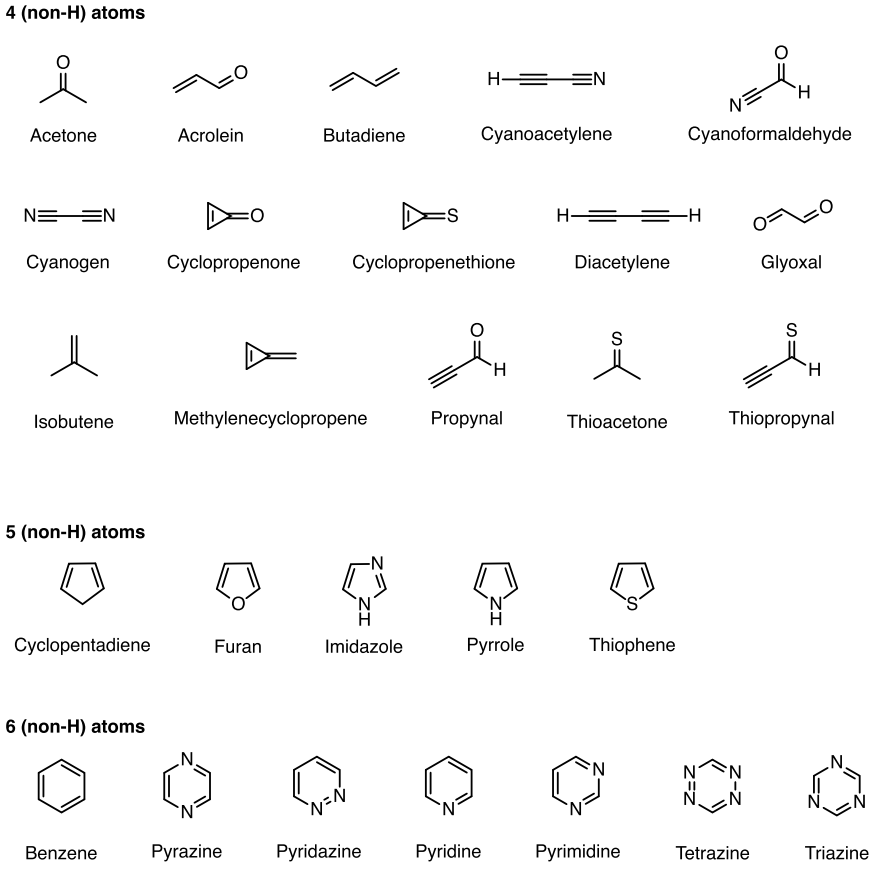
Scheme 1. Representation of the Considered Compounds



we systematically use CC3/aVTZ GS geometries obtained without applying the frozen-core approximation. The Cartesian coordinates (in bohr) of each compound can be found in the Supporting Information (SI). Several structures have been extracted from previous contributions,[75−77] whereas the missing structures were optimized using DALTON[78] and/or CFOUR,[79] applying default parameters in both cases.

2.2. Selected Configuration Interaction. Because SCI methods are less widespread than the other methods mentioned in the Introduction, we shall detail further their main features. All the SCI calculations have been performed in the frozen-core approximation with the latest version of QUANTUM PACKAGE[80] using the Configuration Interaction using a Perturbative Selection made Iteratively (CIPSI) algorithm to select the most important determinants in the FCI space. Instead of generating all possible excited determinants like a conventional CI calculation, the iterative CIPSI algorithm performs a sparse exploration of the FCI space via a selection of the most relevant determinants using a second-order perturbative criterion. At each iteration, the variational (or reference) space is enlarged with new determinants. CIPSI can be seen as a deterministic version of the FCIQMC algorithm developed by Alavi and coworkers.[81] We refer the interested reader to ref 80, where our implementation of the CIPSI algorithm is detailed.

Excited-state calculations are performed within a state-averaged formalism which means that the CIPSI algorithm selects determinants simultaneously for the GS and ESs. Therefore, all electronic states share the same set of determinants with different CI coefficients. Our implementation of the CIPSI algorithm for ES is detailed in ref 82. For each system, a preliminary SCI calculation is performed using Hartree−Fock orbitals in order to generate SCI wave functions with at least 5 000 000 determinants. State-averaged natural orbitals are then computed based on this wave function, and a new, larger SCI calculation is performed with this new set of orbitals. This has the advantage to produce a smoother and faster convergence of the SCI energy toward the FCI limit. For the largest systems, an additional iteration is sometimes required in order to obtain better quality natural orbitals and hence well-converged calculations.

The total SCI energy is defined as the sum of the (zeroth-order) variational energy (computed via diagonalization of the CI matrix in the reference space) and a second-order perturbative correction which takes into account the external determinants, i.e., the determinants which do not belong to the variational space but are linked to the reference space via a nonzero matrix element. The magnitude of this second-order correction, $E^{(2)}$, provides a qualitative idea of the "distance" to the FCI limit. For maximum efficiency, the total SCI energy is linearly extrapolated to $E^{(2)} = 0$ (which effectively corresponds to the FCI limit) using the two largest SCI wave functions. These extrapolated total energies (simply labeled as FCI in the remainder of the paper) are then used to compute vertical excitation energies. Although it is not possible to provide a theoretically sound error bar, we estimate the extrapolation error by the difference in excitation energy between the largest SCI wave function and its corresponding extrapolated value. We believe that it provides a very safe estimate of the extrapolation error. Additional information about the SCI wave functions and excitation energies as well as their extrapolated values can be found in the SI.

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Table 1. Vertical Transition Energies (in eV) of Cyanoacetylene, Cyanogen, and Diacetylene[a]

	Cyanoacetylene														
	6-31+G(d)				aVDZ				aVTZ			aVQZ	aV5Z	lit.	
state	CC3	CCSDT	CCSDTQ	FCI	CC3	CCSDT	CCSDTQ	FCI	CC3	CCSDT	NEVPT2	CC3	CC3	th.[b]	exp.[c]
$^1\Sigma^-$	6.02	6.04	6.02	6.02 ± 0.01	5.92	5.92	5.91	5.84 ± 0.09	5.80	5.81	5.78	5.79	5.79	5.46	4.77
$^1\Delta$	6.29	6.31	6.29	6.28 ± 0.01	6.17	6.19	6.17	6.14 ± 0.05	6.08	6.09	6.10	6.06	6.06	5.81	5.48
$^3\Sigma^+$	4.44	4.45		4.45 ± 0.03	4.43	4.43		4.41 ± 0.06	4.45	4.44	4.45	4.46	4.47		
$^3\Delta$	5.35	5.34		5.32 ± 0.03	5.28	5.27		5.20 ± 0.08	5.22	5.21	5.19	5.22	5.22		
$^1A''$[F][d]	3.70	3.72	3.70	3.67 ± 0.03	3.60	3.62	3.60	3.59 ± 0.02	3.54	3.56	3.50	3.54			
	Cyanogen														
	6-31+G(d)				aVDZ				aVTZ			aVQZ	aV5Z	lit.	
state	CC3	CCSDT	CCSDTQ	FCI	CC3	CCSDT	CCSDTQ	FCI	CC3	CCSDT	NEVPT2	CC3	CC3	exp.[e]	
$^1\Sigma_u^-$	6.62	6.63	6.62	6.58 ± 0.03	6.52	6.52	6.51	6.44 ± 0.08	6.39	6.40	6.32	6.38	6.38	5.63	
$^1\Delta_u$	6.88	6.89	6.88	6.87 ± 0.02	6.77	6.78	6.77	6.74 ± 0.04	6.66	6.67	6.66	6.64	6.64	5.99	
$^3\Sigma_u^+$	4.92	4.92	4.94	4.91 ± 0.06	4.89	4.89		4.87 ± 0.07	4.90	4.89	4.88	4.91	4.91	4.13	
$^1\Sigma_u^-$[F][d]	5.27	5.28	5.26	5.31 ± 0.05	5.19	5.20	5.18	5.26 ± 0.09	5.06	5.07	4.97	5.05	5.05		
	Diacetylene														
	6-31+G(d)				aVDZ				aVTZ			aVQZ	aV5Z	lit.	
state	CC3	CCSDT	CCSDTQ	FCI	CC3	CCSDT	CCSDTQ	FCI	CC3	CCSDT	NEVPT2	CC3	CC3	exp.[f]	
$^1\Sigma_u^-$	5.57	5.58	5.56	5.52 ± 0.06	5.44	5.45	5.43	5.47 ± 0.02	5.34	5.35	5.33	5.33	5.33	4.81	
$^1\Delta_u$	5.83	5.85		5.84 ± 0.01	5.69	5.70	5.69	5.69 ± 0.02	5.61	5.62	5.61	5.60	5.60	5.06	
$^3\Sigma_u^+$	4.07	4.08	4.09	4.04 ± 0.07	4.06	4.06		4.07 ± 0.04	4.08		4.08	4.10	4.11	2.7	
$^3\Delta_u$	4.93	4.93	4.92	4.94 ± 0.01	4.86	4.85		4.85 ± 0.02	4.80	4.79	4.78	4.80	4.80	3.21	

[a]All states have a valence $\pi \rightarrow \pi^*$ character. [b]CASPT2 results from ref 106. [c]Experimental 0-0 energies from refs 107 and 108 (vacuum UV experiments). [d]Vertical fluorescence energy of the lowest excited state. [e]Experimental 0-0 energies from refs 109 ($^3\Sigma_u^+$), 110 ($^1\Sigma_u^-$), and 111 ($^1\Delta_u$), all analyzing vacuum electronic spectra. [f]Experimental 0-0 energies from ref 112 (singlet ES, vacuum UV experiment) and ref 113 (triplet ES, EELS). In the latter contribution, the 2.7 eV value for the $^3\Sigma_u^+$ state is the onset, whereas an estimate of the vertical energy (4.2 ± 0.2 eV) is given for the $^3\Delta_u$ state.

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Table 2. Vertical Transition Energies (in eV) for Cyclopropenone, Cyclopropenethione, and Methylenecyclopropene

Cyclopropenone											
	6-31+G(d)				aVDZ		aVTZ			lit.	
state	CC3	CCSDT	CCSDTQ	FCI	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[a]	exp.[b]
$^1B_1(n \rightarrow \pi^*)$	4.32	4.34	4.36	4.38 ± 0.02	4.22	4.23	4.21	4.24	4.04	4.25	4.13
$^1A_2(n \rightarrow \pi^*)$	5.68	5.65	5.65	5.64 ± 0.06	5.59	5.56	5.57	5.55	5.85	5.59	5.5
$^1B_2(n \rightarrow 3s)$	6.39	6.38	6.41		6.21	6.19	6.32	6.31	6.51	6.90	6.22
$^1B_2(\pi \rightarrow \pi^*)$	6.70	6.67	6.68		6.56	6.54	6.54	6.53	6.82	5.96	6.1
$^1B_2(n \rightarrow 3p)$	6.92	6.91	6.94		6.88	6.86	6.96	6.95	7.07	7.24	6.88
$^1A_1(n \rightarrow 3p)$	7.00	7.00	7.03		6.88	6.87	7.00	6.99	7.28	7.28	
$^1A_1(\pi \rightarrow \pi^*)$	8.51	8.49	8.51		8.32	8.29	8.28	8.26	8.19	7.80	∼8.1
$^3B_1(n \rightarrow \pi^*)$	4.02	4.03		4.00 ± 0.07	3.90	3.92	3.91	3.93	3.51	4.05	
$^3B_2(\pi \rightarrow \pi^*)$	4.92	4.92		4.95 ± 0.00	4.90	4.89	4.89	4.88	5.10	4.81	
$^3A_2(n \rightarrow \pi^*)$	5.48	5.44			5.38	5.35	5.37	5.35	5.60	5.56	
$^3A_1(\pi \rightarrow \pi^*)$	6.89	6.88			6.79	6.78	6.83	6.79	7.16	6.98	

Cyclopropenethione										
	6-31+G(d)				aVDZ		aVTZ			lit.
state	CC3	CCSDT	CCSDTQ	FCI	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[a]
$^1A_2(n \rightarrow \pi^*)$	3.46	3.44	3.44	3.45 ± 0.01	3.47	3.45	3.43	3.41	3.52	3.23
$^1B_1(n \rightarrow \pi^*)$	3.45	3.44	3.45	3.44 ± 0.05	3.42	3.42	3.43	3.44	3.50	3.47
$^1B_2(\pi \rightarrow \pi^*)$	4.67	4.64	4.62	4.59 ± 0.09	4.66	4.64	4.64	4.62	4.77	4.34
$^1B_2(n \rightarrow 3s)$	5.26	5.24	5.27		5.23	5.21	5.34	5.31	5.35	4.98
$^1A_1(\pi \rightarrow \pi^*)$	5.53	5.52	5.51		5.52	5.50	5.49	5.47	5.54	5.52
$^1B_2(n \rightarrow 3p)$	5.83	5.81	5.83		5.86	5.84	5.93	5.90	5.99	5.88
$^3A_2(n \rightarrow \pi^*)$	3.33	3.31		3.29 ± 0.03	3.34	3.32	3.30		3.38	3.20
$^3B_1(n \rightarrow \pi^*)$	3.34	3.33			3.30	3.30	3.31	3.32	3.40	3.30
$^3B_2(\pi \rightarrow \pi^*)$	4.01	4.00		4.03 ± 0.03	4.03	4.02	4.02		4.17	3.86
$^3A_1(\pi \rightarrow \pi^*)$	4.06	4.04			4.09	4.07	4.03		4.13	3.99

Methylenecyclopropene												
	6-31+G(d)				aVDZ		aVTZ			lit.		
state	CC3	CCSDT	CCSDTQ	FCI	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[c]	th.[d]	exp.[e]
$^1B_2(\pi \rightarrow \pi^*)$	4.38	4.37	4.34	4.32 ± 0.03	4.32	4.31	4.31	4.31	4.37	4.13	4.36	4.01
$^1B_1(\pi \rightarrow 3s)$	5.65	5.66	5.66		5.35	5.35	5.44	5.44	5.49	5.32	5.44	5.12
$^1A_2(\pi \rightarrow 3p)$	5.97	5.98	5.98	5.92 ± 0.10	5.86	5.88	5.95	5.96	6.00	5.83		
$^1A_1(\pi \rightarrow \pi^*)$[f]	6.17	6.18	6.17	6.20 ± 0.01	6.15	6.15	6.13	6.13	6.36		6.13	6.02
$^3B_2(\pi \rightarrow \pi^*)$	3.50	3.50		3.44 ± 0.06	3.49	3.49[g]	3.50	3.49	3.66	3.24		
$^3A_1(\pi \rightarrow \pi^*)$	4.74	4.74		4.67 ± 0.10	4.74	4.74[g]	4.74		4.87	4.52		

[a]CASPT2 results from ref 124. [b]Electron impact experiment from ref 126. Note that the 5.5 eV peak was assigned differently in the original paper, and we follow here the analysis of Serrano-Andrés,[124] whereas the 6.1 eV assignment was "supposed" in the original paper; experimental λ_{max} values have been measured at 3.62 and 6.52 eV for the $^1B_1(n \rightarrow \pi^*)$ and $^1B_2(\pi \rightarrow \pi^*)$ transitions, respectively.[127] [c]CASPT2 results from refs 35 and 37. [d]CC3 results from ref 27. [e]λ_{max} in pentane at −78 °C from ref 128. [f]Significant state mixing with the $^1A_1(\pi \rightarrow 3p)$ transition, making unambiguous attribution difficult. [g]As can be seen in the SI, our FCI/aVDZ estimates are 3.45 ± 0.04 and 4.79 ± 0.02 eV for the two lowest triplet states of methylenecyclopropene hinting that the CC3 and CCSDT results might be slightly too low for the second transition.

2.3. NEVPT2. The NEVPT2 calculations have been performed with MOLPRO[83] within the partially contracted scheme (PC-NEVPT2), which is theoretically superior to its strongly contracted version due to the larger number of perturbers and greater flexibility.[84−86] These NEVPT2 calculations are performed on top of a state-averaged complete-active-space self-consistent field calculation always including at least the ground state with the excited state of interest. Active spaces carefully chosen and tailored for the desired transitions have been selected. The definition of the active space considered for each system as well as the number of states in the state-averaged calculation are provided in the SI.

2.4. Other Wave Function Calculations. For the other levels of theory, we apply a variety of programs, namely, CFOUR,[79] DALTON,[78] GAUSSIAN,[87] ORCA,[88] MRCC,[89,90] and Q-CHEM.[91] CFOUR is used for CC3,[92,93] CCSDT-3,[94,95] CCSDT,[96] and CCSDTQ;[97] DALTON for CC2,[98,99] CCSD,[100] CCSDR(3),[101] and CC3;[92,93] GAUSSIAN for CIS(D);[102,103] ORCA for the similarity-transformed (ST) equation-of-motion (EOM) CCSD (STEOM-CCSD);[66,104] MRCC for CCSDT[96] and CCSDTQ;[97] and Q-CHEM for ADC(2).[105] Default program settings were applied. We note that for STEOM-CCSD we only report states that are characterized by an active character percentage of 98% or larger. In all the softwares mentioned above, point group symmetry was systematically employed to reduce the computational effort. It should be noted that we do not perform "GS" CC calculations in a specific symmetry to deduce ES energies. All the CC results reported below correspond to excited-state calculations within the EOM or linear-response (LR) formalisms, both delivering strictly

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identical results for transition energies. These formalisms are also applied to get the triplet ES energies directly from the closed-shell singlet GS. In other words, all our calculations systematically consider a restricted closed-shell ground state. Finally, the reported CC3 oscillator strengths have been determined within the LR formalism.

3. MAIN RESULTS

In the following, we present results obtained for molecules containing four, five, and six (non-hydrogen) atoms. In all cases, we test several atomic basis sets and push the CC excitation order as high as technically possible. Given that the SCI energy converges rather slowly for these systems, we provide an estimated error bar for these extrapolated FCI values (*vide supra*). In most cases, these extrapolated FCI reference data are used as a "safety net" to demonstrate the overall consistency of the various approaches rather than as definitive reference values (see the next section). As a further consistency check, we also report NEVPT2/aVTZ excitation energies for all states. We underline that, except when specifically discussed, all ESs present a dominant single-excitation character (see also next section) so that we do not expect serious CC breakdowns. This is especially true for triplet ESs that are known to be characterized by very large $\%T_1$ values in the vast majority of the cases.[23] Consequently, we concentrate most of our computational effort on the obtention of accurate transition energies for singlet states. To assign the different ESs, we use literature data, as well as the usual criteria, i.e., relative energies, spatial and spin symmetries, compositions from the underlying molecular orbitals, and oscillator strengths. This allows clear-cut assignments for the vast majority of the cases. There are however some state/method combinations for which strong mixing between ESs of the same symmetry makes unambiguous assignments almost impossible.

3.1. Molecules with Four Non-Hydrogen Atoms.

3.1.1. Cyanoacetylene, Cyanogen, and Diacetylene. The ESs of these three closely related linear molecules containing two triple bonds have been quite rarely theoretically investigated,[106,114−117] though (rather old) experimental measurements of their 0-0 energies are available for several ESs.[107−113,118] Our main results are collected in Tables 1 and S1. We consider only low-lying valence $\pi \rightarrow \pi^*$ transitions, which are all characterized by a strongly dominant single excitation nature ($\%T_1 > 90\%$, *vide infra*). For cyanoacetylene, the FCI/6-31+G(d) estimates come with small error bars, and one notices an excellent agreement between these values and their CCSDTQ counterparts, a statement holding for the Dunning double-ζ basis set results for which the FCI uncertainties are however larger. Using the CCSDTQ values as references, it appears that the previously obtained CASPT2 estimates[106] are, as expected, too low and that the CC3 transition energies are slightly more accurate than their CCSDT counterparts, although all CC estimates of Table 1 come, for a given basis set, in a very tight energetic window. There is also a very neat agreement between the CC/aVTZ and NEVPT2/aVTZ. All these facts provide strong evidence that the CC estimates can be fully trusted for these three linear systems. The basis set effects are quite significant for the valence ES of cyanoacetylene with successive drops of the transition energies by approximately 0.10 eV, when going from 6−31+G(d) to aVDZ and from aVDZ to aVTZ. The lowest triplet state appears less basis set sensitive, though. As expected, extending further the basis set size (to quadruple- and quintuple-ζ) leaves the results pretty much unchanged. The same observation holds when adding a second set of diffuse functions or when correlating the core electrons (see the SI). Obviously, both cyanogen and diacetylene yield very similar trends, with limited methodological effects and quite large basis set effects, except for the $^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ transitions. We note that all CC3 and CCSDT values are, at worst, within ±0.02 eV of the FCI window, i.e., all methods presented in Table 1 provide very consistent estimates. For all the states reported in Table 1, the average absolute deviation between NEVPT2/aVTZ and CC3/aVTZ (CCSDT/aVTZ) is as small as 0.02 (0.03) eV, the lowest absorption and emission energies of cyanogen being the only two cases showing significant deviations. As a final note, all our vertical absorption (emission) energies are significantly larger (smaller) than the experimentally measured 0-0 energies, as they should be. We refer the interested reader to previous works,[114,117] for comparisons between theoretical (CASPT2 and CC3) and experimental 0-0 energies for these three compounds.

3.1.2. Cyclopropenone, Cyclopropenethione, and Methylenecyclopropene. These three related compounds present a three-membered sp^2 carbon cycle conjugated to an external π bond. While the ESs of methylenecyclopropene have regularly been investigated with theoretical tools in the past,[27,35,37,75,119−123] the only investigations of vertical transitions we could find for the two other derivatives are a detailed CASPT2 study of Serrano-Andrés and co-workers in 2002[124] and a more recent work reporting the three lowest-lying singlet states of cyclopropenone at the CASPT2/6-31G level.[125]

Our results are listed in Tables 2 and S2. As above, considering the 6-31+G(d) basis set, we notice very small differences between CC3, CCSDT, and CCSDTQ, the latter method giving transition energies systematically falling within the FCI extrapolation incertitude, except in one case (the lowest totally symmetric state of methylenecyclopropene for which the CCSDTQ value is "off" by 0.02 eV only). Depending on the state, it is either CC3 or CCSDT that is closest to CCSDTQ. In fact, considering the CCSDTQ/6-31+G(d) data listed in Table 2 as reference, the MAEs of CC3 and CCSDT are 0.019 and 0.016 eV, respectively, hinting that the improvement brought by the latter, more expensive method is limited for these three compounds. For the lowest B_2 state of methylenecyclopropene, one of the most challenging cases ($\%T_1 = 85\%$), it is clear from the FCI value that only CCSDTQ is energetically close, the CC3 and CCSDT results being slightly too large by ∼0.05 eV. It seems reasonable to believe that the same observation can be made for the corresponding state of cyclopropenethione, although in this case the FCI error bar is too large, which prevents any definitive conclusion. Interestingly, at the CC3 level of theory, the rather small 6-31+G(d) basis set provides data within 0.10 eV of the CBS limit for 80% of the transitions. There are, of course, exceptions to this rule, e.g., the strongly dipole-allowed $^1A_1(\pi \rightarrow \pi^*)$ ES of cyclopropenone and the $^1B_1(\pi \rightarrow 3s)$ ES of methylenecyclopropene which are significantly over blueshifted with the Pople basis set (Table S2). For cyclopropenone, our CCSDT/aVTZ estimates do agree reasonably well with the CASPT2 data of Serrano-Andrés, except for the $^1B_2(\pi \rightarrow \pi^*)$ state that we locate significantly higher in energy and the three Rydberg states that our CC calculations predict at significantly lower energies. The present NEVPT2 results are globally in better agreement with the CC values, though non-negligible deviations pertain. Even if comparisons with experiment should be made very cautiously, we note that, for the Rydberg states, the present CC data are

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Table 3. Vertical Transition Energies (in eV) of Acrolein, Butadiene, and Glyoxal

	Acrolein										
	6-31+G(d)			aVDZ		aVTZ			lit.		
state	CC3	CCSDT	FCI	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[a]	th.[b]	exp.[c]
$^1A''(n \rightarrow \pi^*)$	3.83	3.80	3.85 ± 0.01	3.77	3.74	3.74	3.73	3.76	3.63	3.83	3.71
$^1A'(\pi \rightarrow \pi^*)$	6.83	6.86	6.59 ± 0.05[f]	6.67	6.70	6.65	6.69	6.67	6.10	6.92	6.41
$^1A''(n \rightarrow \pi^*)$	6.94	6.89		6.75	6.72	6.75		7.16	6.26	7.40	
$^1A'(n \rightarrow 3s)$	7.22	7.23		6.99	7.00	7.07		7.05	6.97	7.19	7.08
$^3A''(n \rightarrow \pi^*)$	3.55	3.53	3.60 ± 0.01	3.47	3.45	3.46		3.46	3.39	3.61	
$^3A'(\pi \rightarrow \pi^*)$	3.94	3.95	3.98 ± 0.03	3.95	3.95	3.94		3.95	3.81	3.87	
$^3A'(\pi \rightarrow \pi^*)$	6.25	6.23		6.22	6.21	6.19		6.23		6.21	
$^3A''(n \rightarrow \pi^*)$	6.81	6.74		6.60		6.61		6.83		7.36	
	Butadiene										
	6-31+G(d)				aVDZ		aVTZ			lit.	
state	CC3	CCSDT	CCSDTQ	FCI	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[b]	th.[d]	exp.[e]
$^1B_u(\pi \rightarrow \pi^*)$	6.41	6.43	6.41	6.41 ± 0.02	6.25	6.27	6.22	6.24	6.68	6.33	6.36	5.92
$^1B_g(\pi \rightarrow 3s)$	6.53	6.55	6.54		6.26	6.27	6.33	6.34	6.44	6.18	6.32	6.21
$^1A_g(\pi \rightarrow \pi^*)$	6.73	6.63	6.56	6.55 ± 0.04[f]	6.68	6.59	6.67	6.60	6.70	6.56	6.60	
$^1A_u(\pi \rightarrow 3p)$	6.87	6.89	6.87		6.57	6.59	6.64	6.66	6.84	6.45	6.56	6.64
$^1A_u(\pi \rightarrow 3p)$	6.93	6.95	6.94	6.95 ± 0.01	6.73	6.74	6.80	6.81	7.01	6.65	6.74	6.80
$^1B_u(\pi \rightarrow 3p)$	7.98	8.00	7.98		7.86	7.87	7.68		7.45	7.08	7.02	7.07
$^3B_u(\pi \rightarrow \pi^*)$	3.35	3.36		3.37 ± 0.03	3.36	3.36	3.36		3.40	3.20		3.22
$^3A_g(\pi \rightarrow \pi^*)$	5.22	5.22			5.21	5.21	5.20		5.30	5.08		4.91
$^3B_g(\pi \rightarrow 3s)$	6.46	6.47		6.40 ± 0.03	6.20	6.21	6.28		6.38	6.14		
	Glyoxal										
	6-31+G(d)				aVDZ		aVTZ			lit.	
state	CC3	CCSDT	CCSDTQ	FCI	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[b]	th.[g]	exp.[h]
$^1A_u(n \rightarrow \pi^*)$	2.94	2.94	2.94	2.93 ± 0.03	2.90	2.90	2.88	2.88	2.90	3.10	2.93	2.8
$^1B_g(n \rightarrow \pi^*)$	4.34	4.32	4.31	4.28 ± 0.06	4.30	4.28	4.27	4.25	4.30	4.68	4.39	~4.4
$^1A_g(n, n \rightarrow \pi^*,\pi^*)$	6.74	6.24	5.67	5.60 ± 0.09[f]	6.70	6.22	6.76	6.35	5.52	5.66		
$^1B_g(n \rightarrow \pi^*)$	6.81	6.83	6.79		6.59	6.61	6.58	6.61	6.64	7.54	6.63	7.45
$^1B_u(n \rightarrow 3p)$	7.72	7.74	7.76		7.55	7.56	7.67	7.69	7.84	7.83	7.61	~7.7
$^3A_u(n \rightarrow \pi^*)$	2.55	2.55		2.54 ± 0.04	2.49	2.49	2.49	2.49	2.49	2.63		2.5
$^3B_g(n \rightarrow \pi^*)$	3.97	3.95			3.91	3.90	3.90	3.89	3.99	4.12		~3.8
$^3B_u(\pi \rightarrow \pi^*)$	5.22	5.20			5.20	5.19	5.17	5.15	5.17	5.35		~5.2
$^3A_g(\pi \rightarrow \pi^*)$	6.35	6.35			6.34	6.34	6.30	6.30	6.33			

[a]CASPT2 results from ref 129. [b]SAC-CI results from ref 130. [c]Vacuum UV spectra from ref 150; for the lowest state, the same 3.71 eV value is reported in ref 151. [d]MR-AQCC results from ref 134, with theoretical best estimates listed for the lowest B_u and A_g states. [e]Electron impact experiment from refs 152 and 153 for the singlet states and from ref 154 for the two lowest triplet transitions; note that, for the lowest B_u state, there is a vibrational structure with peaks at 5.76, 5.92, and 6.05 eV. [f]From ref 72. [g]CC3 results from ref 27. [h]Electron impact experiment from ref 155 except for the second ^1B_g ES for which the value is from another work (see ref 156); note that for the lowest $^1B_g(^1B_u)$ ES, a range of 4.2−4.5 (7.4−7.9) eV is given in ref 155.

clearly more consistent with the electron impact measurements[126] than the original CASPT2 values. For cyclopropenethione, we typically obtain transition energies in agreement with or larger than those obtained with CASPT2,[124] though there is no obvious relationship between the valence/Rydberg nature of the ES and the relative CASPT2 error. The average absolute deviation between our NEVPT2 and CC3 results is 0.08 eV only. Finally, in the case of methylenecyclopropene, our values logically agree very well with the recent estimates of Schwabe and Goerigk,[27] obtained at the CC3/aVTZ level of theory on a different geometry. As anticipated, the available CASPT2 values,[35,37] determined without IPEA shift, appear too low as compared to the present NEVPT2 and CCSDT values. For this compound, the available experimental data are based on the wavelength of maximal absorption determined in the condensed phase.[128] Hence, only a qualitative match is reached between theory and experiment.

3.1.3. Acrolein, Butadiene, and Glyoxal. Let us now turn our attention to the excited states of three pseudolinear π-conjugated systems that have been the subject to several investigations in the past, namely, acrolein,[27,119−121,129−133] butadiene,[23,26,27,72,120,130,134−145] and glyoxal.[27,116,120,130,132,146−149] Among these works, it is worth highlighting the detailed theoretical investigation of Saha, Ehara, and Nakatsuji, who reported a huge number of ESs for these three systems using a coherent theoretical protocol based on the symmetry-adapted-cluster configuration interaction (SAC-CI) method.[130] In the following, these three molecules are considered in their most stable *trans* conformation. Our results are listed in Tables 3 and S3.

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Table 4. Vertical Transition Energies (in eV) of Acetone, Cyanoformaldehyde, Isobutene, Propynal, Thioacetone, and Thiopropynal

	Acetone											
	6-31+G(d)				aVDZ		aVTZ			lit.		
state	CC3	CCSDT	CCSDTQ	FCI	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[a]	th.[b]	exp.[c]
$^1A_2(n \rightarrow \pi^*)$	4.55	4.52	4.53	4.60 ± 0.05	4.50	4.48	4.48	4.46	4.48	4.18	4.18	4.48
$^1B_2(n \rightarrow 3s)$	6.65	6.64	6.68		6.31	6.30	6.43	6.42	6.81	6.58	6.58	6.36
$^1A_2(n \rightarrow 3p)$	7.83	7.83	7.87		7.37	7.36	7.45	7.43	7.65	7.34	7.34	7.36
$^1A_1(n \rightarrow 3p)$	7.81	7.81	7.84		7.39	7.38	7.48	7.48	7.75	7.26	7.26	7.41
$^1B_2(n \rightarrow 3p)$	7.87	7.87	7.91		7.56	7.55	7.59	7.58	7.91	7.48	7.48	7.45
$^3A_2(n \rightarrow \pi^*)$	4.21	4.19		4.18 ± 0.04	4.16	4.14	4.15		4.20	3.90	3.90	4.15
$^3A_1(\pi \rightarrow \pi^*)$	6.32	6.30			6.31	6.28	6.28		6.28	5.98	5.98	
	Cyanoformaldehyde											
	6-31+G(d)			aVDZ		aVTZ				lit.		
state	CC3	CCSDT	FCI	CC3	CCSDT	CC3	CCSDT	NEVPT2		exp.[d]		
$^1A''(n \rightarrow \pi^*)$	3.91	3.89	3.92 ± 0.02	3.86	3.84	3.83	3.81	3.98		3.26		
$^1A''(\pi \rightarrow \pi^*)$	6.64	6.67	6.60 ± 0.07	6.51	6.54	6.42	6.46	6.44				
$^3A''(n \rightarrow \pi^*)$	3.53	3.51	3.48 ± 0.06	3.47	3.45	3.46		3.58				
$^3A'(\pi \rightarrow \pi^*)$	5.07	5.07		5.03	5.03	5.01		5.35				
	Isobutene											
	6-31+G(d)			aVDZ		aVTZ			lit.			
state	CC3	CCSDT	FCI	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[e]	exp.[f]	exp.[g]	
$^1B_1(\pi \rightarrow 3s)$	6.77	6.77	6.78 ± 0.08	6.39	6.39	6.45	6.46	6.63	6.40	6.15	6.17	
$^1A_1(\pi \rightarrow 3p)$	7.16	7.17	7.16 ± 0.02	7.00	7.00	7.00	7.01	7.20	6.96		6.71	
$^3A_1(\pi \rightarrow \pi^*)$	4.52	4.53	4.56 ± 0.02	4.54	4.54	4.53		4.61		4.21	4.3	
	Propynal											
	6-31+G(d)			aVDZ		aVTZ				lit.		
state	CC3	CCSDT	FCI	CC3	CCSDT	CC3	CCSDT	NEVPT2		exp.[h]		
$^1A''(n \rightarrow \pi^*)$	3.90	3.87	3.84 ± 0.06	3.85	3.82	3.82	3.80	3.95		3.24		
$^1A''(\pi \rightarrow \pi^*)$	5.69	5.73	5.64 ± 0.08	5.59	5.62	5.51	5.54	5.50				
$^3A''(n \rightarrow \pi^*)$	3.56	3.54	3.54 ± 0.04	3.50	3.48	3.49		3.59		2.99		
$^3A'(\pi \rightarrow \pi^*)$	4.46	4.47	4.44 ± 0.08	4.40	4.44	4.43		4.63				
	Thioacetone											
	6-31+G(d)				aVDZ		aVTZ			lit.		
state	CC3	CCSDT	CCSDTQ	FCI	CC3	CCSDT	CC3	CCSDT	NEVPT2	exp.[i]		
$^1A_2(n \rightarrow \pi^*)$	2.58	2.56	2.56	2.61 ± 0.05	2.59	2.57	2.55	2.53	2.55	2.33		
$^1B_2(n \rightarrow 4s)$	5.65	5.64	5.66		5.44	5.43	5.55	5.54	5.72	5.49		
$^1A_1(\pi \rightarrow \pi^*)$	6.09	6.10	6.07		5.97	5.98	5.90	5.91	6.24	5.64		
$^1B_2(n \rightarrow 4p)$	6.59	6.59	6.59		6.45	6.44	6.51		6.62	6.40		
$^1A_1(n \rightarrow 4p)$	6.95	6.95	6.96		6.54	6.53	6.61	6.60	6.52	6.52		
$^3A_2(n \rightarrow \pi^*)$	2.36	2.34		2.36 ± 0.00	2.36	2.35	2.34		2.32	2.14		
$^3A_1(\pi \rightarrow \pi^*)$	3.45	3.45			3.51	3.50	3.46		3.48			
	Thiopropynal											
	6-31+G(d)			aVDZ		aVTZ				lit.		
state	CC3	CCSDT	FCI	CC3	CCSDT	CC3	CCSDT	NEVPT2		exp.[j]		
$^1A''(n \rightarrow \pi^*)$	2.09	2.06	2.08 ± 0.01	2.09	2.06	2.05	2.03	2.05		1.82		
$^3A''(n \rightarrow \pi^*)$	1.84	1.82		1.83	1.82	1.81		1.81		1.64		

[a]CASPT2 results from ref 36. [b]EOM-CCSD results from ref 157. [c]Two lowest singlet states: various experiments summarized in ref 169; three next singlet states: REMPI experiments from ref 172; lowest triplet: trapped electron measurements from ref 166. [d]0-0 energy reported in ref 171. [e]EOM-CCSD results from ref 160. [f]Energy loss experiment from ref 167. [g]VUV experiment from ref 170 (we report the lowest of the $\pi \rightarrow 3p$ state for the $^1A_1$ state). [h]0-0 energies from refs 165 (singlet) and 163 (triplet). [i]0-0 energies from ref 164. [j]0-0 energies from ref 168.

Acrolein, due to its lower symmetry and high density of ES with mixed characters, is challenging from a theoretical point of view, and CCSDTQ calculations were technically impossible despite all our efforts. For the lowest $n \rightarrow \pi^*$ transitions of both spin symmetries, the FCI estimates come with a tiny error bar, and it is obvious that the CC excitation energies are slightly too low, especially with CCSDT. Nevertheless, at the exception of the second singlet and triplet A'' ESs, the CC3 and CCSDT transition energies are within ±0.03 eV of each other. These A'' ESs are also the only two transitions for which the discrepancies

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between CC3 and NEVPT2 exceed 0.20 eV. This hints at a good accuracy for all other transitions. This statement is additionally supported by the fact that the present CC values are nearly systematically bracketed by previous CASPT2 (lower bound)[129] and SAC-CI (upper bound)[130] results, consistently with the typical error sign of these two models. For the two lowest triplet states, the present CC3/aVTZ values are also within ±0.05 eV of the recent MRCI estimates (3.50 and 3.89 eV).[131] As can be seen in Table S3, the aVTZ basis set delivers excitation energies very close to the CBS limit: the largest variation when upgrading from aVTZ to aVQZ (+0.04 eV) is obtained for the second $^1A'$ Rydberg ES. As experimental data are limited to measured UV spectra,[150,151] one has to be ultra cautious in establishing TBEs for acrolein (*vide infra*).

The nature and relative energies of the lowest bright B_u and dark A_g ESs of butadiene have puzzled theoretical chemists for many years. It is beyond the scope of the present study to provide an exhaustive list of previous calculations and experimental measurements for these two hallmark ESs, and we refer the readers to refs 137 and 141 for a general and broader overview. For the B_u transition, we believe that the most solid TBE is the 6.21 eV value obtained by Watson and Chan using a computational strategy similar to ours.[137] Our CCSDT/aVTZ value of 6.24 eV is obviously compatible with their reference value, and our TBE/CBS value is actually 6.21 eV as well (*vide infra*). For the A_g state, we believe that our previous basis set corrected FCI estimate of 6.50 eV[72] remains the most accurate available to date. These two values are slightly lower than the semistochastic heath-bath CI data obtained by Chien et al. with a double-ζ basis and a slightly different geometry: 6.45 and 6.58 eV for B_u and A_g, respectively.[143] For these two thoroughly studied ESs, one can of course find many other estimates, e.g., at the SAC-CI,[130] CC3,[26,27] CASPT2,[26] and NEVPT2[142] levels. Globally, for butadiene, we find an excellent coherence between the CC3, CCSDT, and CCSDTQ estimates, that all fall in a ±0.02 eV window. Unsurprisingly, this does not apply to the already mentioned ^1A_g ES that is, respectively, 0.2 and 0.1 eV too high with the two former CC methods, a direct consequence of the large electronic reorganization taking place during this transition. For all the other butadiene ESs listed in Table 3, both CC3 and CCSDT can be trusted. We also note that the NEVPT2 estimates are within 0.1−0.2 eV of the CC values, except for the lowest B_u ES for which the associated excitation energy is highly dependent on the selected active space (see the SI). Finally, as can be seen in Table S3, aVTZ produces near-CBS excitation energies for most ESs. However, a significant basis set effect exists for the Rydberg $^1B_u(\pi \rightarrow 3p)$ ES with an energy lowering as large as −0.12 eV when going from aVTZ to aVQZ. For the record, we note that the available electron impact data[152−154] provides the very same ES ordering as our calculations.

Globally, the conclusions obtained for acrolein and butadiene pertain for glyoxal, i.e., highly consistent CC estimates, reasonable agreement between NEVPT2 and CC3 values, and limited basis set effects beyond aVTZ, except for the ^1B_u ($n \rightarrow 3p$) Rydberg state (see Tables 3 and S3). This Rydberg state also exhibits an unexpectedly large deviation of 0.04 eV between CC3 and CCSDTQ. More interestingly, glyoxal presents a genuine low-lying double ES of ^1A_g symmetry. The corresponding $(n, n) \rightarrow (\pi^*, \pi^*)$ transition is totally unseen by approaches that cannot model double excitations, e.g., TD-DFT, CCSD, or ADC(2). Compared to the FCI values, the CC3 and CCSDT estimates associated with this transition are too large by ∼1.0 and ∼0.5 eV, respectively, whereas both the CCSDTQ and the NEVPT2 approaches are much closer, as already mentioned in our previous work.[72] For the other transitions, the present CC3 estimates are logically consistent with the values of ref 27 obtained with the same approach on a different geometry and remain slightly lower than the SAC-CI estimates of ref 130. Once more, the experimental data[155,156] are unhelpful in view of the targeted accuracy.

3.1.4. Acetone, Cyanoformaldehyde, Isobutene, Propynal, Thioacetone, and Thiopropynal. Let us now turn toward six other compounds with four non-hydrogen atoms. There are several earlier studies reporting estimates of the vertical transition energies for both acetone[23,26,27,36,37,39,121,139,157−161] and isobutene.[139,159,160] To the best of our knowledge, for the four other compounds, the previous computational efforts were mainly focused on the 0-0 energies of the lowest-lying state.[116,117,147,148,162] There are also rather few experimental data available for these six derivatives.[163,164,166−172] Our main results are reported in Tables 4 and S4.

For acetone, one should clearly distinguish the valence ES, for which both methodological and basis set effects are small, and the Rydberg transitions that are both very basis set sensitive and upshifted by ca. 0.04 eV with CCSDTQ as compared to CC3 and CCSDT. For this compound, the 1996 CASPT2 transition energies of Merchán and co-workers listed on the right panel of Table 4 are clearly too low, especially for the three valence ESs.[36] As expected, this error can be partially ascribed to the computational setup, as the Urban group obtained CASPT2 excitation energies of 4.40, 4.09, and 6.22 eV for the $^1A_2$, $^3A_2$, and $^3A_1$ ESs,[161] in much better agreement with ours. Their estimates of the three $n \rightarrow 3p$ transitions, 7.52, 7.57, and 7.53 eV for the $^1A_2$, $^1A_1$, and $^1B_2$ ESs, also systematically fall within 0.10 eV of our current CC values, whereas for these three ESs, the current NEVPT2 values are clearly too large.

In contrast to acetone, both valence and Rydberg ESs of thioacetone are rather insensitive to the excitation order of the CC expansion as illustrated by the maximal discrepancies of ±0.02 eV between the CC3/6-31+G(d) and CCSDTQ/6-31+G(d) results. While the lowest $n \rightarrow \pi^*$ transition of both spin symmetries are rather basis set insensitive, all the other states need quite large one-electron bases to be correctly described (Table S4). As expected, our theoretical vertical transition energies show the same ranking but are systematically larger than the available experimental 0-0 energies.

For the isoelectronic isobutene molecule, we have considered two singlet Rydberg ESs and one triplet valence ES. For these three cases, we note, for each basis, a very nice agreement between CC3 and CCSDT, the CC results being also very close to the FCI estimates obtained with the Pople basis set. The similarity with the CCSD results of Caricato and co-workers[160] is also very satisfying.

For the three remaining compounds, namely, cyanoformaldehyde, propynal, and thiopropynal, we report low-lying valence transitions with a definite single excitation character. The basis set effects are clearly under control (they are only significant for the second $^1A''$ ES of cyanoformaldehyde), and we could not detect any variation larger than 0.03 eV between the CC3 and the CCSDT values for a given basis, indicating that the CC values are very accurate. This is further confirmed by the FCI data.

3.1.5. Intermediate Conclusions. For the 15 molecules with four non-hydrogen atoms considered here, we find extremely consistent transition energies between CC and FCI estimates in

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Table 5. Vertical Transition Energies (in eV) of Furan and Pyrrole

	Furan												
	6-31+G(d)		aVDZ		aVTZ			lit.					
state	CC3	CCSDT	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[a]	th.[b]	th.[c]	th.[d]	th.[e]	exp.[f]	exp.[g]
$^1A_2(\pi \rightarrow 3s)$	6.26	6.28	6.00	6.00	6.08	6.09	6.28	5.92	6.13	5.94	5.91	6.10	5.91	
$^1B_2(\pi \rightarrow \pi^*)$	6.50	6.52	6.37	6.39	6.34	6.37	6.20	6.04	6.42	6.51	6.10	6.42	6.04	6.06
$^1A_1(\pi \rightarrow \pi^*)$	6.71	6.67	6.62	6.58	6.58	6.56	6.77	6.16	6.71	6.89	6.44			6.44
$^1B_1(\pi \rightarrow 3p)$	6.76	6.77	6.55	6.56	6.63	6.64	6.71	6.46	6.68	6.46	6.45	6.66	6.47	
$^1A_2(\pi \rightarrow 3p)$	6.97	6.99	6.73	6.74	6.80	6.81	6.99	6.59	6.79	6.61	6.60	6.83	6.61	
$^1B_2(\pi \rightarrow 3p)$	7.53	7.54	7.39	7.40	7.23		7.01	6.48	6.91	6.87	6.72	7.36	6.75	
$^3B_2(\pi \rightarrow \pi^*)$	4.28	4.28	4.25	4.23	4.22		4.42	3.99		4.26				4.0
$^3A_1(\pi \rightarrow \pi^*)$	5.56	5.54	5.51	5.49	5.48		5.60	5.15		5.53				5.2
$^3A_2(\pi \rightarrow 3s)$	6.18	6.19	5.94	5.94	6.02		6.08	5.86		5.89				
$^3B_1(\pi \rightarrow 3p)$	6.69	6.71	6.51	6.51	6.59		6.68	6.42		6.41				
	Pyrrole												
	6-31+G(d)		aVDZ		aVTZ			lit.					
state	CC3	CCSDT	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[a]	th.[h]	th.[c]	th.[i]	th.[j]	exp.[k]	exp.[l]
$^1A_2(\pi \rightarrow 3s)$	5.25	5.25	5.15	5.14	5.24	5.24	5.51	5.08	5.45	5.10	5.20	5.27	5.22	
$^1B_1(\pi \rightarrow 3p)$	5.99	5.98	5.89	5.87	5.98	6.00	6.32	5.85	6.21	5.79	5.95	6.00		
$^1A_2(\pi \rightarrow 3p)$	6.27	6.27	5.94	5.93	6.01		6.44	5.83	6.14	5.81	5.94	7.03		5.87
$^1B_2(\pi \rightarrow \pi^*)$	6.33	6.33	6.28	6.28	6.25	6.26	6.48	5.92	6.95	5.96	6.04	6.08		5.98
$^1A_1(\pi \rightarrow \pi^*)$	6.43	6.40	6.35	6.32	6.32	6.30	6.53	5.92	6.59	6.53	6.37	6.15		
$^1B_2(\pi \rightarrow 3p)$	7.20	7.20	7.00	7.00	6.83		6.62	5.78	6.26	6.61	6.57			
$^3B_2(\pi \rightarrow \pi^*)$	4.59	4.58	4.56	4.54	4.53		4.74	4.27		4.53			4.21	
$^3A_2(\pi \rightarrow 3s)$	5.22	5.22	5.12	5.12	5.21		5.49	5.04		5.07			5.1	
$^3A_1(\pi \rightarrow \pi^*)$	5.54	5.54	5.49	5.48	5.46		5.56	5.16		5.53				
$^3B_1(\pi \rightarrow 3p)$	5.91	5.90	5.82	5.81	5.92		6.28	5.82		5.74				

[a]CASPT2 results from ref 32. [b]NEVPT2 results from ref 180. [c]MR-CC results from ref 182. [d]ADC(3) results from ref 184. [e]CC3 results from ref 27. [f]Various experiments summarized in ref 178. [g]Electron impact from ref 185: for the $^1A_1$ state two values (6.44 and 6.61 eV) are reported, whereas for the two lowest triplet states, two values (3.99 and 5.22 eV) can be found in ref 186. [h]NEVPT2 results from ref 187. [i]Best estimate from ref 188, based on CC calculations. [j]XMS-CASPT2 results from ref 189. [k]Electron impact from refs 185 and 190. [l]Vapor UV spectra from refs 191, 192, and 193.

the vast majority of the cases. Importantly, we confirm our previous conclusions obtained on smaller compounds:[28] (i) CCSDTQ values systematically fall within (or are extremely close to) the FCI error bar, and (ii) both CC3 and CCSDT are also highly trustable when the considered ES does not exhibit a strong double excitation character. Indeed, considering the 54 "single" ES cases for which CCSDTQ estimates could be obtained (only excluding the lowest ^1A_g ES of butadiene and glyoxal), we determined negligible MSE < 0.01 eV, tiny MAE (0.01 and 0.02 eV), and small maximal deviations (0.05 and 0.04 eV) for CC3 and CCSDT, respectively. This clearly indicates that these two approaches provide chemically accurate estimates (errors below 1 kcal·mol^{-1} or 0.043 eV) for most electronic transitions. Interestingly, some of us have shown that CC3 also provides chemically accurate 0-0 energies as compared to experimental values for most valence transitions.[116,117,173] When comparing the NEVPT2 and CC3 (CCSDT) results obtained with aVTZ for the 91 (65) ESs for which comparisons are possible (again excluding only the lowest ^1A_g states of butadiene and glyoxal), one obtains an MSE of +0.09 (+0.09) eV and an MAE of 0.11 (0.12) eV. This seems to indicate that NEVPT2, as applied here, has a slight tendency to overestimate the transition energies. This contrasts with "standard" CASPT2 which is known to generally underestimate transition energies, as further illustrated and discussed above and below.

3.2. Five-Membered Rings. We now consider five-membered rings, and, in particular, five common derivatives that have been considered in several previous theoretical studies (*vide infra*): cyclopentadiene, furan, imidazole, pyrrole, and thiophene. As the most advanced levels of theory employed in the previous section, namely, CCSDTQ and FCI, become beyond reach for these compounds (except in very rare occasions), one has to rely on the nature of the ES and the consistency between results to deduce TBEs.

For furan, *ab initio* calculations have been performed with almost every available wave function method.[23,25−27,32,174−184] However, the present work is, to the best of our knowledge, the first to disclose CCSDT values as well as CC3 energies obtained with a quadruple-ζ basis set. Our results for 10 low-lying ES states are listed in Tables 5 and S5. All singlet (triplet) transitions are characterized by %T_1 values in the 92−94% (97−99%) range. Consistently, the maximal discrepancy between CC3 and CCSDT is small (0.04 eV). In addition, there is a decent consistency between the present data and the NEVPT2 results of both ref 180 and of the present work, as well as the MR-CC values of ref 182. This holds for almost all transitions except the $^1B_2(\pi \rightarrow 3p)$ excitation that we predict to be significantly higher than in most previous works, even after accounting for the quite large basis set effects (−0.10 eV between the aVTZ and aVQZ estimates, see Table S5). We believe that our estimate is the most accurate to date for this particularly tricky ES. Interestingly, the recent ADC(3) values of ref 184 are consistently smaller by ca. −0.2 eV as compared to CCSDT (see Table 6), in agreement with the error sign we observed in

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Table 6. Vertical Transition Energies (in eV) of Cyclopentadiene, Imidazole, and Thiophene

Cyclopentadiene														
	6-31+G(d)		aVDZ		aVTZ			lit.						
state	CC3	CCSDT	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[a]	th.[b]	th.[c]	th.[d]	exp.[e]	exp.[f]	exp.[g]
$^1B_2(\pi \rightarrow \pi^*)$	5.79	5.80	5.59	5.60	5.54	5.56	5.65	5.27	5.54	5.19	5.58	5.26		5.20
$^1A_2(\pi \rightarrow 3s)$	6.08	6.08	5.70	5.70	5.77	5.78	5.92	5.65	5.58	5.62	5.79	5.68	5.63	
$^1B_1(\pi \rightarrow 3p)$	6.57	6.58	6.34	6.34	6.40	6.41	6.42	6.24	6.17	6.24	6.43		6.35	
$^1A_2(\pi \rightarrow 3p)$	6.67	6.67	6.39	6.39	6.45	6.46	6.59	6.30	6.21	6.25	6.47			6.26
$^1B_2(\pi \rightarrow 3p)$	7.06	7.07	6.55	6.55	6.56	6.56	6.60	6.25	6.22	6.27	6.58		6.31	
$^1A_1(\pi \rightarrow \pi^*)$	6.67	6.60	6.59	6.53	6.57	6.52	6.75	6.31	6.76	6.42	6.65			~6.2
$^3B_2(\pi \rightarrow \pi^*)$	3.33	3.33	3.32	3.31	3.32		3.41	3.15	3.40			3.10		
$^3A_1(\pi \rightarrow \pi^*)$	5.16	5.15	5.14	5.13	5.12		5.30	4.90	5.18			>4.7		
$^3A_2(\pi \rightarrow 3s)$	6.01	6.02	5.65	5.65	5.73		5.73	5.63	5.56					
$^3B_1(\pi \rightarrow 3p)$	6.51	6.52	6.30	6.30	6.36		6.40	6.25	6.19					

Imidazole									
	6-31+G(d)		aVDZ		aVTZ		lit.		
state	CC3	CCSDT	CC3	CCSDT	CC3	NEVPT2	th.[h]	th.[i]	exp.[j]
$^1A''(\pi \rightarrow 3s)$	5.77	5.77	5.60	5.60	5.71	5.93	5.71		~5.2
$^1A'(\pi \rightarrow \pi^*)$[k]	6.51	6.51	6.43	6.43	6.41	6.73	6.72	6.25	~6.4
$^1A''(n \rightarrow \pi^*)$	6.66	6.66	6.42	6.42	6.50	6.96	6.52	6.65	
$^1A'(\pi \rightarrow 3p)$[k]	7.04	7.02	6.93	6.89	6.87	7.00	6.49		
$^3A'(\pi \rightarrow \pi^*)$	4.83	4.81	4.78		4.75	4.86	4.49	4.65	
$^3A''(\pi \rightarrow 3s)$	5.72	5.72	5.57	5.56	5.67	5.91	5.68		
$^3A'(\pi \rightarrow \pi^*)$	5.88	5.88	5.78		5.74	5.91	5.47	5.64	
$^3A''(n \rightarrow \pi^*)$	6.48	6.46	6.37	6.35	6.33	6.48	6.07	6.25	

Thiophene														
	6-31+G(d)		aVDZ		aVTZ			lit.						
state	CC3	CCSDT	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[l]	th.[m]	th.[n]	th.[o]	exp.[p]	exp.[q]	exp.[r]
$^1A_1(\pi \rightarrow \pi^*)$	5.79	5.77	5.70	5.68	5.65	5.64	5.84	5.33	5.41	5.70	5.64	5.16	5.13	5.16
$^1B_2(\pi \rightarrow \pi^*)$	6.23	6.24	6.05	6.06	5.96	5.98	6.10	5.72	5.72	6.10	5.97	5.99	5.83	
$^1A_2(\pi \rightarrow 3s)$	6.26	6.26	6.07	6.06	6.14	6.14	6.20	5.93	5.70	6.05	6.23			
$^1B_1(\pi \rightarrow 3p)$	6.18	6.17	6.19	6.17	6.14	6.14	6.19	6.30	5.87	6.30	6.17			6.71
$^1A_2(\pi \rightarrow 3p)$	6.32		6.33	6.31	6.25	6.21	6.40	6.35	6.03	6.28	6.33			
$^1B_1(\pi \rightarrow 3s)$	6.62	6.62	6.42	6.41	6.50	6.49	6.71	6.23	6.12	6.36	6.68			6.47
$^1B_2(\pi \rightarrow 3p)$[s]	7.45	7.44	7.45	7.44	7.29	7.29	7.25	6.56	6.41	6.81	6.97			6.60
$^1A_1(\pi \rightarrow \pi^*)$	7.50	7.46	7.41		7.35		7.39	6.69	7.32	7.71	7.74	6.61		
$^3B_2(\pi \rightarrow \pi^*)$	3.95	3.94	3.96	3.94	3.94		4.13	3.75	3.94		3.96		3.74	
$^3A_1(\pi \rightarrow \pi^*)$	4.90	4.90	4.82	4.81	4.77		4.84	4.50	4.86		4.87		4.62	
$^3B_1(\pi \rightarrow 3p)$	6.00	5.98	6.01	5.99	5.95		5.98	5.90	5.94		6.01			
$^3A_2(\pi \rightarrow 3s)$	6.20	6.20	6.01	6.00	6.09		6.14	5.88	5.75		5.83			

[a]CASPT2 results from ref 32. [b]SAC-CI results from ref 198. [c]MR-MP results from ref 174. [d]CC3 results from ref 27. [e]Electron impact from ref 199. [f]Gas phase absorption from ref 200. [g]Energy loss from ref 201 for the two valence states; two-photon resonant experiment from ref 202 for the $^1A_2$ Rydberg ES. [h]CASPT2 results from ref 38. [i]CC3 results from ref 26. [j]Gas-phase experimental estimates from ref 203. [k]The assignments of these two states as valence and Rydberg are based on the oscillator strength, but both have a partial Rydberg character. The CASSCF spatial extent is in fact larger for the lowest transition, and Roos consequently classified both ESs as Rydberg transitions.[38] [l]CASPT2 results from ref 33. [m]SAC-CI results from ref 204. [n]CCSDR(3) results from ref 205. [o]TBE from ref 206, based on EOM-CCSD for the singlet and ADC(2) for triplets. [p]0-0 energies from ref 207. [q]0-0 energies from ref 208 for the singlets and energy loss experiment from ref 209 for the triplets. [r]0-0 energies from ref 206. [s]Non-negligible mixing with a close-lying $(\pi \rightarrow \pi^*)$ transition of the same symmetry.

smaller compounds for ADC(3).[28] Again, we note that the experimental data[156,185,186] provide the same state ordering as our calculations.

Like furan, pyrrole has been extensively investigated in the literature using a large panel of theoretical methods.[23,25−27,32,174,178,181−183,187−189,191,194−197] We report six low-lying singlet and four triplet ESs in Tables 5 and S5. All these transitions have very large $\%T_1$ values except for the totally symmetric $\pi \rightarrow \pi^*$ excitation ($\%T_1$ = 86%). For each state, we found highly consistent CC3 and CCSDT results, often significantly larger than older multireference estimates[32,182,196] but in nice agreement with the very recent XMS-CASPT2 results of the González group,[189] and the present NEVPT2 estimates [at the exception of the $^1A_2(\pi \rightarrow 3p)$ transition]. The match obtained with the 20 years old extrapolated CC values of Christiansen and co-workers[188] is quite remarkable. The only exceptions are the two B_2 transitions that were reported as significantly mixed in this venerable work. For the lowest singlet ES, the FCI/6-31+G(d) value is 5.24 ± 0.02 eV confirming the performance of both CC3 and CCSDT for this transition. As can

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Table 7. Vertical Transition Energies (in eV) of Benzene

	6-31+G(d)		aVDZ		aVTZ			lit.					
state	CC3	CCSDT	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[a]	th.[b]	th.[c]	th.[d]	exp.[e]	exp.[f]
$^1B_{2u}(\pi \rightarrow \pi^*)$	5.13	5.10	5.11	5.08	5.09	5.06	5.32	4.84	5.08	5.06	5.03		4.90
$^1B_{1u}(\pi \rightarrow \pi^*)$	6.68	6.69	6.50	6.50	6.44	6.45	6.43	6.30	6.54	6.22	6.23		6.20
$^1E_{1g}(\pi \rightarrow 3s)$	6.75	6.76	6.46	6.46	6.52	6.52	6.75	6.38	6.51	6.42			6.33
$^1A_{2u}(\pi \rightarrow 3p)$	7.24	7.25	7.02	7.02	7.08	7.08	7.40	6.86	6.97	7.06			6.93
$^1E_{2u}(\pi \rightarrow 3p)$	7.34	7.35	7.09	7.09	7.15	7.15	7.45	6.91	7.03	7.12			6.95
$^3B_{1u}(\pi \rightarrow \pi^*)$	4.18	4.16	4.19	4.17	4.18		4.32	3.89	4.15	3.88	4.11	3.95	
$^3E_{1u}(\pi \rightarrow \pi^*)$	4.95	4.94	4.89	4.88	4.86		4.92	4.49	4.86	4.72	4.75	4.75	
$^3B_{2u}(\pi \rightarrow \pi^*)$	6.06	6.06	5.86	5.86	5.81		5.51	5.49	5.88	5.54	5.67	5.60	

[a]CASPT2 results from ref 34. [b]CC3 results from ref 215. [c]SAC-CI results from ref 218. [d]RASPT2(18,18) results from ref 220. [e]Electron impact from ref 221. [f]Jet-cooled experiment from ref 225 for the two lowest states, and multiphoton experiments from refs 223 and 224 for the Rydberg states.

be seen in Table S5, aVTZ yields basis-set converged transition energies, except, like in furan, for the Rydberg $^1B_2(\pi \rightarrow 3p)$ transition that is significantly red-shifted (−0.09 eV) when pushing to the quadruple-ζ basis set. As mentioned in Thiel's work,[23] the experimental spectra of pyrrole are quite broad, and the rare available experiments[185,190−193,195] can only be considered as general guidelines.

Although diverse wave function studies have been performed on cyclopentadiene (including CASPT2,[23,26,32] CC,[23,25,27] SAC-CI,[198] and various multireference approaches[174,181]), this compound has received less attention than other members of the five-membered ring family, namely, furan and pyrrole (*vide infra*). This is probably due to the presence of the methylene group that renders computations significantly more expensive. Most transitions listed in Tables 6 and S6 are characterized by %T_1 exceeding 93%, the only exception being the $^1A_1(\pi \rightarrow \pi^*)$ excitation that has a similar nature as the lowest A_g state of butadiene (%T_1 = 79%). Consistently, the CC3 and CCSDT results are nearly identical for all ESs except for the $^1A_1$ ES. By comparing the results obtained for this $A_1(\pi \rightarrow \pi^*)$ transition to its butadiene counterpart, one can infer that the CCSDT estimate is probably too large by roughly 0.04−0.08 eV and that the NEVPT2 value is unlikely to be accurate enough to establish a definitive TBE. This statement is also in line with the results of ref 72. For the two $B_2(\pi \rightarrow \pi^*)$ transitions, we could obtain FCI/6-31+G(d) estimates of 5.78 ± 0.02 eV (singlet) and 3.33 ± 0.05 eV (triplet), the CC3 and CCSDT transition energies falling inside these energetic windows in both cases. As one can see in Tables 6 and S6, the basis set effects are rather moderate for the electronic transitions of cyclopentadiene, with no variation larger than 0.10 eV (0.02 eV) between aVDZ and aVTZ (aVTZ and aVQZ). When comparing to literature data, our values are unsurprisingly consistent with the CC3 values of Schwabe and Goerigk[27] and tend to be significantly larger than earlier CASPT2[26,32] and MR-MP[174] estimates. As expected, a few gas-phase experiments are available as well for this derivative,[199−202] but they hardly represent grounds for comparison.

Due to its lower symmetry, imidazole has been less investigated, the most advanced studies available probably remain the CASPT2 work of Serrano-Andrès and co-workers from 1996,[38] and the basis-set extrapolated CC3 results of Silva-Junior et al. for the valence transitions from 2010.[26] The experimental data in gas-phase are also limited.[203] Our results are displayed in Tables 6 and S6. The CC3 and CCSDT values are quite consistent despite the fact that the %T_1 values of the two singlet A' states are slightly smaller than 90%. These two states have indeed, at least partially, a Rydberg character (see the footnote in Table 6). The agreement between the CC estimates and previous CASPT2,[38] and current NEVPT2 energies is reasonable, the latter being systematically larger than their CC3 counterparts. For the eight transitions considered here, the basis set effects are moderate and aVTZ yield results within 0.03 eV of their aVQZ counterparts (Table S6 in the SI).

Finally, the ESs of thiophene, which is one of the most important building block in organic electronic devices, were the subject of previous theoretical investigations[33,204−206,210,211] that unveiled a series of transitions that were not yet characterized in the available measurements.[186,190,206−210] To the best of our knowledge, the present work is the first to report CC calculations obtained with (iterative) triples and therefore constitutes the most accurate estimates to date. Indeed, all the transitions listed in Tables 6 and S6 are characterized by a largely dominant single excitation character, with %T_1 above 90% except for the two $^1A_1$ transitions for which %T_1 = 88% and 87%. The agreement between CC3 and CCSDT remains nevertheless excellent for these low-lying totally symmetric transitions. Thiophene is also one of these compounds for which the unambiguous characterization of the nature of the ES is difficult, with, e.g., a strong mixing between the second and third singlet ESs of B_2 symmetry. This makes the assignment of the valence $(\pi \rightarrow \pi^*)$ or Rydberg $(\pi \rightarrow 3p)$ character of this transition particularly tricky at the CC3 level. We note that contradictory assignments can be found in the literature.[33,204,205] As for the previously discussed isostructural systems, the only ES that undergoes significant basis set effects beyond aVTZ is the Rydberg $^1B_2(\pi \rightarrow 3p)$ (−0.09 eV when upgrading to aVQZ, see Table S6) and that the NEVPT2 estimates tend to be slightly larger than the CC3 values. The data of Table 6 are globally in good agreement with the previously reported values with discrepancies that are significant only for the three highest-lying singlet states.

3.3. Six-Membered Rings. Let us now turn toward seven six-membered rings which play a key role in chemistry: benzene, pyrazine, pyridazine, pyridine, pyrimidine, tetrazine, and triazine. To the best of our knowledge, the present work is the first to propose CCSDT reference energies as well as CC3/aVQZ values for all these compounds. Of course, these systems have been investigated before, and beyond Thiel's benchmarks,[23,25,26] it is worth pointing out the early investigation of Del Bene and co-workers[212] performed with a CC approach including perturbative corrections for the triples. Following a theoretically consistent protocol, Nooijen[213] also performed STEOM-CCSD calculations to study the ESs of each of these

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Table 8. Vertical Transition Energies (in eV) of Pyrazine and Tetrazine

Pyrazine													
	6-31+G(d)		aVDZ		aVTZ			lit.					
state	CC3	CCSDT	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[a]	th.[b]	th.[c]	th.[d]	exp.[e]	exp.[f]
$^1B_{3u}(n \rightarrow \pi^*)$	4.28	4.28	4.19	4.19	4.14	4.15	4.17	3.83	4.12	4.25	4.19	3.93	
$^1A_u(n \rightarrow \pi^*)$	5.08	5.08	4.98	4.98	4.97	4.98	4.77	4.36	4.93	5.24	4.93		
$^1B_{2u}(\pi \rightarrow \pi^*)$	5.10	5.08	5.07	5.05	5.03	5.02	5.32	4.79	4.75	4.84	5.19	4.8	4.81
$^1B_{2g}(n \rightarrow \pi^*)$	5.86	5.85	5.78	5.77	5.71	5.71	5.88	5.50	5.85	6.04	5.81	5.19	
$^1A_g(n \rightarrow 3s)$	6.74	6.73	6.54	6.53	6.66	6.65	6.70		6.83	7.07	6.46		
$^1B_{1g}(n \rightarrow \pi^*)$	6.87	6.87	6.75	6.75	6.73	6.74	6.75	6.26	6.73		6.73		6.10
$^1B_{1u}(\pi \rightarrow \pi^*)$	7.10	7.11	6.92	6.93	6.86	6.88	6.81	6.60	6.89	6.68	6.99	6.5	6.51
$^1B_{1g}(\pi \rightarrow 3s)$	7.36	7.37	7.13	7.14	7.20	7.21	7.33		7.31	7.08			
$^1B_{2u}(n \rightarrow 3p)$	7.39	7.39	7.14	7.13	7.25		7.25		7.45	7.67	7.06		
$^1B_{1u}(n \rightarrow 3p)$	7.56	7.55	7.38	7.37	7.45		7.42	7.28	7.50	7.73	7.31		7.67
$^1B_{1u}(\pi \rightarrow \pi^*)$	8.19	8.23	7.99	8.03	7.94		8.25	7.43	7.96	8.24	8.08		
$^3B_{3u}(n \rightarrow \pi^*)$	3.68	3.68	3.60	3.60	3.59		3.56	3.16				3.33	
$^3B_{1u}(\pi \rightarrow \pi^*)$	4.39	4.36	4.40	4.36	4.39		4.57	4.15				4.04	
$^3B_{2u}(\pi \rightarrow \pi^*)$	4.56	4.55	4.46	4.45	4.40		4.42	4.28				~4.4	
$^3A_u(n \rightarrow \pi^*)$	5.05	5.05	4.93	4.93	4.93		4.75	4.19				4.2	
$^3B_{2g}(n \rightarrow \pi^*)$	5.18	5.17	5.11	5.11	5.08		5.21	4.81				4.49	
$^3B_{1u}(\pi \rightarrow \pi^*)$	5.38	5.37	5.32	5.31	5.29		5.35	4.98					
Tetrazine													
	6-31+G(d)		aVDZ		aVTZ			lit.					
state	CC3	CCSDT	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[g]	th.[h]	th.[i]	th.[j]	th.[k]	exp.[l]
$^1B_{3u}(n \rightarrow \pi^*)$	2.53	2.54	2.49	2.50	2.46	2.47	2.35	1.96	2.22	2.01	2.29	2.46	2.35
$^1A_u(n \rightarrow \pi^*)$	3.75	3.75	3.69	3.70	3.67	3.69	3.58	3.06	3.62	3.09	3.41	3.78	3.6
^1A_g(double)[m]	6.22	5.86	6.22	5.86	6.21	5.96	4.61	4.37	5.06	4.34	4.66		
$^1B_{1g}(n \rightarrow \pi^*)$	5.01	5.02	4.97	4.98	4.91	4.93	4.95	4.51	4.73	4.47	4.53	4.87	
$^1B_{2u}(\pi \rightarrow \pi^*)$	5.29	5.26	5.27	5.25	5.23	5.21	5.56	4.89	4.90		5.59	5.08	4.97
$^1B_{2g}(n \rightarrow \pi^*)$	5.56	5.52	5.53	5.50	5.46	5.45	5.63	5.05	5.09	4.92	5.59	5.28	
$^1A_u(n \rightarrow \pi^*)$	5.61	5.61	5.59	5.59	5.52	5.53	5.62	5.28	5.23	5.32	5.95	5.39	5.5
$^1B_{3g}$(double)[m]	7.64		7.62		7.62		6.15	5.16	6.30	5.26	6.01		5.92
$^1B_{2g}(n \rightarrow \pi^*)$	6.24	6.22	6.17	6.16	6.13		6.13	5.48	6.16	5.78	6.05	6.16	
$^1B_{1g}(n \rightarrow \pi^*)$	7.04	7.04	6.98	6.98	6.92		6.76	5.99	6.73	6.20	6.92	6.80	
$^3B_{3u}(n \rightarrow \pi^*)$	1.87	1.88	1.86	1.86	1.85		1.73	1.45	1.71			1.87	1.7
$^3A_u(n \rightarrow \pi^*)$	3.48	3.49	3.43	3.44	3.44		3.36	2.81	3.47			3.49	2.90
$^3B_{1g}(n \rightarrow \pi^*)$	4.25	4.25	4.23	4.23	4.20		4.24	3.76	3.97			4.18	
$^3B_{1u}(\pi \rightarrow \pi^*)$	4.54	4.49	4.54	4.49	4.54		4.70	4.25	3.67			4.36	
$^3B_{2u}(\pi \rightarrow \pi^*)$	4.65	4.64	4.58	4.58	4.52		4.58	4.29	4.35			4.39	
$^3B_{2g}(n \rightarrow \pi^*)$	5.11	5.11	5.09	5.08	5.05		5.27	4.67	4.78			4.89	
$^3A_u(n \rightarrow \pi^*)$	5.17	5.17	5.15	5.15	5.11		5.13	4.85	4.89			4.96	
$^3B_{3g}$(double)[m]	7.35		7.33		7.35		5.51	5.08					
$^3B_{1u}(\pi \rightarrow \pi^*)$	5.51	5.50	5.46	5.46	5.42		5.56	5.09	5.31			5.32	

[a]CASPT2 results from ref 226. [b]STEOM-CCSD results from ref 213. [c]SAC-CI results from ref 218. [d]CC3 results from ref 27. [e]Double resonance dip spectroscopy from ref 235 (B_{3u} and B_{2g} ESs) and EEL from ref 236 (others). [f]UV max from ref 234.. [g]CASPT2 results from ref 229. [h]Ext-STEOM-CCSD results from ref 231. [i]GVVPT2 results from ref 219. [j]NEVPT2 results from ref 232. [k]CC3 results from ref 26. [l]From ref 238, the singlets are from EEL, except for the 4.97 and 5.92 eV values that are from VUV; the triplets are from EEL, and additional (unassigned) triplet peaks are found at 4.21, 4.6, and 5.2 eV. [m]All these three doubly ESs have a (n, $n \rightarrow \pi^*$, π^*) character.

derivatives. However, these two works only considered singlet ESs.

3.3.1. Benzene, Pyrazine, and Tetrazine. These three highly symmetric systems allow CCSDT/aVTZ calculations for singlet states to be directly performed without the need of basis set extrapolations. Benzene was studied many times before,[23,25−27,34,66,69,72,120,136,183,212−220] and we report in Tables 7 and S7 estimates obtained for five singlet and three triplet ESs, all characterized by %T_1 exceeding 90% except for the lowest singlet (86%). As one can see, the two CC approaches are again yielding very consistent transition energies with variations in the 0.00−0.03 eV range. Besides, aVTZ essentially provides basis set converged transition energies (Table S7). The present CC estimates are also very consistent with earlier CC3 results[215] and are compatible with both the very recent RASPT2[220] and our NEVPT2 values. For the states of both spin symmetries, the CC3 and CCSDT transitions energies are slightly larger than the available electron impact/multiphoton measurements[221−225] but do provide energetic gaps between ESs very similar to the measured ones.

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Table 9. Vertical Transition Energies (in eV) of Pyridazine and Pyridine

Pyridazine												
	6-31+G(d)		aVDZ		aVTZ		lit.					
state	CC3	CCSDT	CC3	CCSDT	CC3	NEVPT2	th.[a]	th.[b]	th.[c]	th.[d]	exp.[e]	exp.[f]
$^1B_1(n \rightarrow \pi^*)$	3.95	3.95	3.86	3.86	3.83	3.80	3.48	3.76	3.65	3.85		3.36
$^1A_2(n \rightarrow \pi^*)$	4.49	4.48	4.39	4.39	4.37	4.40	3.66	4.46	4.28	4.44		4.02
$^1A_1(\pi \rightarrow \pi^*)$	5.36	5.32	5.33	5.30	5.29	5.58	4.86	4.92	4.86	5.20	5.0	5.01
$^1A_2(n \rightarrow \pi^*)$	5.88	5.86	5.80	5.78	5.74	5.88	5.09	5.66	5.52	5.66		5.61
$^1B_2(n \rightarrow 3s)$	6.26	6.27	6.06	6.06	6.17	6.21		6.45				
$^1B_1(n \rightarrow \pi^*)$	6.51	6.51	6.41	6.41	6.37	6.64	5.80	6.41	6.20	6.33		6.00
$^1B_2(\pi \rightarrow \pi^*)$	6.96	6.97	6.79	6.80	6.74	7.10	6.61	6.77	6.44	6.68		6.50
$^3B_1(n \rightarrow \pi^*)$	3.27	3.26	3.20	3.20	3.19	3.13						3.06
$^3A_2(n \rightarrow \pi^*)$	4.19	4.19	4.11	4.11	4.11	4.14						3.55
$^3B_2(\pi \rightarrow \pi^*)$	4.39	4.36	4.39	4.35	4.38	4.49					4.0	4.33
$^3A_1(\pi \rightarrow \pi^*)$	4.93	4.94	4.87	4.86	4.83	4.94					4.4	4.68
Pyridine												
	6-31+G(d)		aVDZ		aVTZ		lit.					
state	CC3	CCSDT	CC3	CCSDT	CC3	NEVPT2	th.[g]	th.[b]	th.[c]	th.[d]	exp.[h]	exp.[i]
$^1B_1(n \rightarrow \pi^*)$	5.12	5.10	5.01	5.00	4.96	5.15	4.91	4.90	4.80	4.95	5.24	4.78
$^1B_2(\pi \rightarrow \pi^*)$	5.23	5.20	5.21	5.18	5.17	5.31	4.84	4.82	4.81	5.12	4.99	4.99
$^1A_2(n \rightarrow \pi^*)$	5.55	5.54	5.41	5.41	5.40	5.29	5.17	5.31	5.24	5.41	5.43	5.40
$^1A_1(\pi \rightarrow \pi^*)$	6.84	6.84	6.64	6.63	6.63	6.69	6.42	6.62	6.36	6.60	6.38	
$^1A_1(n \rightarrow 3s)$	6.92	6.92	6.71	6.71	6.76	6.99	6.70	6.96	6.64		6.28	6.25
$^1A_2(\pi \rightarrow 3s)$	6.98	6.99	6.74	6.75	6.81	6.86	6.75	6.90	6.53			
$^1B_2(\pi \rightarrow \pi^*)$[j]	7.50	7.52	7.40	7.42	7.38	7.83	7.48	7.29	7.14	7.33	7.22	7.20
$^1B_1(\pi \rightarrow 3p)$	7.54	7.55	7.32	7.32	7.38	7.45	7.25	7.42	7.10			
$^1A_1(\pi \rightarrow \pi^*)$	7.56		7.34	7.34	7.39	6.97	7.23	7.37	7.26	7.39	7.22	6.39
$^3A_1(\pi \rightarrow \pi^*)$	4.33	4.31	4.34	4.31	4.33	4.60	4.05			4.28		3.86
$^3B_1(n \rightarrow \pi^*)$	4.57	4.56	4.47	4.47	4.46	4.58	4.41			4.42		4.12
$^3B_2(\pi \rightarrow \pi^*)$	4.92	4.91	4.83	4.83	4.79	4.88	4.56			4.72		4.47
$^3A_1(\pi \rightarrow \pi^*)$	5.14	5.13	5.08		5.05	5.19	4.73			4.96		
$^3A_2(n \rightarrow \pi^*)$	5.51	5.49	5.37	5.36	5.35	5.33	5.10			5.53		5.40
$^3B_2(\pi \rightarrow \pi^*)$	6.46	6.45	6.30	6.29	6.25	6.29	6.02			6.22		6.09

[a]CASPT2 results from ref 30. [b]STEOM-CCSD results from ref 213. [c]EOM-CCSD($\tilde{T}$) from ref 212. [d]CC3-ext. from ref 26. [e]EEL from ref 239. [f]EEL from ref 240. [g]CASPT2 from ref 241. [h]EEL from ref 242. [i]EEL from ref 243. [j]Significant state mixing with a close-lying Rydberg transition making unambiguous attribution difficult. At the CC3/aVDZ level, the Rydberg state is at 7.26 eV and has a small *f*, so attribution is rather clear. However, at the CC3/aVTZ level, the two B_2 transitions are at 7.35 and 7.38 eV (hence strongly mixed), so that the attribution has been made using the *f* values of 0.174 and 0.319, respectively.

There are many available studies of the ESs of pyrazine[23,24,26,27,30,66,69,120,160,183,212,213,218,226,227] and tetrazine,[23−27,66,69,120,160,212,213,228−233] for which the D_{2h} symmetry helps distinguish the different ESs. Our results are collected in Tables 8 and S8. In pyrazine, all transitions are characterized by $\%T_1 > 85\%$ at the exception of the $^1B_{1g}(n \rightarrow \pi^*)$ transition (84%). The excitation energies are basically unchanged going from CC3 to CCSDT except possibly for the highest-lying singlet state considered here. Going from triple- to quadruple-ζ basis, the variations do not exceed 0.04 eV, even for the four Rydberg ESs treated here. This indicates that one can be highly confident in the present estimates except for the highest-lying singlet ES. Again, the previous CASPT2 estimates[23,30,183,226] appear to be globally too low, while the (unconventional) CASPT3 results[227] seem too high. A similar overestimation can be noticed in previous SAC-CI results[218] and our NEVPT2 values, the latter showing a mean absolute deviation of 0.11 eV compared to CC3. In fact, the most satisfying agreement between the current estimates and previous works is reached with Nooijen's STEOM-CCSD values (except for the highest ES),[213] and the recent Schwabe−Goerigk's CC3 estimates.[27] The available experimental data[234−237] do not include all theoretically predicted transitions but provide a similar energetic ranking for both singlets and triplets.

For tetrazine, we consider valence ESs only, including three transitions exhibiting a genuine double excitation nature ($\%T_1 <$ 10%). Of course, for these double excitations, CC3 and CCSDT cannot be considered as reliable. This is illustrated by the large change in excitation energies between these two CC models. The theoretical best estimates are likely obtained with NEVPT2.[72] For all the other transitions, the $\%T_1$ values are in the 80−90% range for singlets and larger than 95% for triplets. Consequently, the CC3 and CCSDT results are very consistent, the sole exception being the lowest $^3B_{1u}(\pi \rightarrow \pi^*)$ transition for which we note a shift of −0.05 eV when upgrading the level of theory to CCSDT. In all other cases, there is a global consistency between our CC values. Moreover, the basis set effects are very small beyond aVTZ with a maximal variation of 0.02 eV when going to aVQZ (Table S8). The present values are almost systematically larger than the previous CASPT2,[229] STEOM-CCSD,[231] and GVVPT2[219] estimates. Our NEVPT2 values are also globally consistent with the CC3 values with a maximal

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Table 10. Vertical Transition Energies (in eV) of Pyrimidine and Triazine

Pyrimidine												
	6-31+G(d)		aVDZ		aVTZ		lit.					
state	CC3	CCSDT	CC3	CCSDT	CC3	NEVPT2	th.[a]	th.[b]	th.[c]	th.[d]	exp.[e]	exp.[f]
$^1B_1(n \rightarrow \pi^*)$	4.58	4.57	4.48	4.48	4.44	4.55	4.26	4.40	4.32	4.24	4.2	4.18
$^1A_2(n \rightarrow \pi^*)$	4.99	4.99	4.89	4.88	4.86	4.84	4.49	4.72	4.74	4.74		4.69
$^1B_2(\pi \rightarrow \pi^*)$	5.47	5.44	5.44	5.41	5.41	5.53	5.47	5.04	5.29	5.01	5.12	5.18
$^1A_2(n \rightarrow \pi^*)$	6.07	6.06	5.98	5.97	5.93	6.02		5.94	5.98	5.84	6.05	5.67
$^1B_1(n \rightarrow \pi^*)$	6.39		6.29	6.29	6.26	6.40	6.03	6.18	6.35	6.11		6.02
$^1B_2(n \rightarrow 3s)$	6.81	6.80	6.61	6.59	6.72	6.77		6.85	6.84	6.57		
$^1A_1(\pi \rightarrow \pi^*)$	7.08	7.09	6.93	6.94	6.87	7.11	7.10	6.87	6.86	6.57	6.7	6.69
$^3B_1(n \rightarrow \pi^*)$	4.20	4.20	4.12	4.11	4.10	4.17	3.81		4.11			3.85
$^3A_1(\pi \rightarrow \pi^*)$	4.55	4.52	4.56	4.52	4.55	4.67	4.35		4.39			4.42
$^3A_2(n \rightarrow \pi^*)$	4.77	4.76	4.67	4.67	4.66	4.72	4.24		4.71			4.18
$^3B_2(\pi \rightarrow \pi^*)$	5.08	5.08	5.00	5.00	4.96	5.01	4.83		4.81			4.93
Triazine												
	6-31+G(d)		aVDZ		aVTZ		lit.					
state	CC3	CCSDT	CC3	CCSDT	CC3	CCSDT	NEVPT2	th.[g]	th.[b]	th.[d]	th.[h]	exp.[e]
$^1A_1''(n \rightarrow \pi^*)$	4.85	4.84	4.76	4.74	4.73	4.72	4.61	4.11	4.58	4.49	4.70	
$^1A_2''(n \rightarrow \pi^*)$	4.84	4.84	4.78	4.78	4.74	4.75	4.89	4.30	4.74	4.54	4.71	4.59
$^1E''(n \rightarrow \pi^*)$	4.89	4.89	4.82	4.81	4.78	4.78	4.88	4.32	4.69	4.56	4.75	3.97
$^1A_2'(\pi \rightarrow \pi^*)$	5.84	5.80	5.81	5.78	5.78	5.75	5.95	5.59	5.35	5.36	5.71	5.70
$^1A_1'(\pi \rightarrow \pi^*)$	7.45	7.45	7.31	7.31	7.24	7.24	7.30		7.21	6.90	7.18	6.86
$^1E'(n \rightarrow 3s)$	7.44	7.41	7.24	7.21	7.35	7.32	7.45		7.38	7.16		
$^1E''(n \rightarrow \pi^*)$	7.89	7.86	7.82	7.80	7.79	7.78	7.98			7.78	7.78	
$^1E'(\pi \rightarrow \pi^*)$	8.12	8.13	7.97		7.92	7.94	8.34		7.82	7.72	7.84	7.76
$^3A_2''(n \rightarrow \pi^*)$	4.40	4.40	4.35	4.35	4.33		4.51	3.87				
$^3E''(n \rightarrow \pi^*)$	4.59	4.59	4.52	4.52	4.51		4.61	4.04				
$^3A_1''(n \rightarrow \pi^*)$	4.87		4.78	4.76	4.75		4.71	4.15				
$^3A_1'(\pi \rightarrow \pi^*)$	4.88	4.85	4.88	4.85	4.88		5.05					
$^3E'(\pi \rightarrow \pi^*)$	5.70	5.68	5.64		5.61		5.73					
$^3A_2'(\pi \rightarrow \pi^*)$	6.85	6.84	6.69	6.68	6.63		6.36	4.76				

[a]CASPT2 results from ref 251. [b]STEOM-CCSD results from ref 213. [c]SAC-CI results from ref 218. [d]EOM-CCSD($\tilde{T}$) results from ref 212. [e]UV max from ref 234. [f]EEL from ref 253. [g]CASPT2 results from ref 255. [h]CC3-ext. results from ref 26.

discrepancy of 0.22 eV for the ESs with a dominant single excitation character. One finds a global agreement with Thiel's CC3/aVTZ values,[26] although we note variations of approximately 0.20 eV for specific excitations like the B_{2g} transitions. This feature might be due to the use of distinct geometries in the two studies. The experimental EEL values from Palmer's work[238] show a reasonable agreement with our estimates.

3.3.2. Pyridazine, Pyridine, Pyrimidine, and Triazine. Those four azabenzenes with a C_{2v} or D_{3h} spatial symmetry are also popular molecules in terms of ES calculations.[23,25−27,30,66,69,104,120,160,183,212,213,239,241,244−247] Our results for pyridazine and pyridine are gathered in Tables 9 and S9. For the former compound, the available wave function results[23,25−27,30,66,69,212,213,239,245] focused on singlet transitions, at the exception of rather old MRCI,[239] and CASPT2 investigations.[245] Again, the $\%T_1$ values are larger than 85% (95%) for the singlet (triplet) transitions, and the only state for which there is a variation larger than 0.03 eV between the CC3/aVDZ and the CCSDT/aVDZ energies is the $^3B_2(\pi \rightarrow \pi^*)$ transition. As in the previous six-membered cycles, the basis set effects are rather small, and aVTZ provides values close to the CBS limit for the considered transitions. For the singlet valence ESs, we find again a rather good match with the results of previous STEOM-CCSD[213] and CC[26,212] calculations. Yet again, these values are significantly higher than the CASPT2 estimates reported in refs 30 and 26. For the triplets, the present data represent the most accurate results published to date. Our NEVPT2 values are very close to their CC3 analogues for the lowest-lying singlet and triplet but positively deviate for the higher-lying ES. Interestingly, beyond the popular 20 year old reference measurements,[239,248] there is a very recent experimental EEL analysis for pyridazine[240] that locates almost all the ESs. The transition energies reported in this very recent work are systematically smaller than our CC estimates by approximately −0.20 eV. Nonetheless, this study provides exactly the same ES ranking as our theoretical protocol.

Pyridine, the hallmark organic heterocycle, has been more scrutinized than pyridazine, and many wave function approaches have been applied to estimate its ES energies.[23,25−27,30,66,69,104,160,183,212,213,241,246,247] Besides, two detailed EEL experiments are also available for pyridine.[242,243] The general trends described above for other six-membered cycles do pertain with (i) large $\%T_1$ values and a nice consistency between CC3 and CCSDT estimates for all transitions listed in Table 9; (ii) small basis set effects beyond aVTZ even for the Rydberg transitions; (iii) qualitative agreement with past CC results; (iv) NEVPT2 transitions energies that are, on average, larger than their CC counterparts; and (v) the same ES ranking as in the most recent measurements.[243] Beyond these aspects, it is worth mentioning that the second $^1B_2(\pi \rightarrow \pi^*)$ ES is strongly mixed

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Table 11. TBE Values (in eV) for All Considered States alongside Their Corresponding Oscillator Strength, *f*, and Percentage of Single Excitations, $\%T_1$, Obtained at the CC3/aVTZ level[a]

				TBE/aVTZ		TBE/CBS	
	state	*f*	$\%T_1$	value	protocol[b]	value	corr.
acetone	$^1A_2$(V; $n \rightarrow \pi^*$)		91.1	4.47	B	4.48	aVQZ
	$^1B_2$(R; $n \rightarrow 3s$)	0.000	90.5	6.46	B	6.51	aVQZ
	$^1A_2$(R; $n \rightarrow 3p$)		90.9	7.47	B	7.44	aVQZ
	$^1A_1$(R; $n \rightarrow 3p$)	0.004	90.6	7.51	B	7.55	aVQZ
	$^1B_2$(R; $n \rightarrow 3p$)	0.029	91.2	7.62	B	7.63	aVQZ
	$^3A_2$(V; $n \rightarrow \pi^*$)		97.8	4.13	D	4.15	aVQZ
	$^3A_1$(V; $\pi \rightarrow \pi^*$)		98.7	6.25	D	6.27	aVQZ
acrolein	$^1A''$(V; $n \rightarrow \pi^*$)	0.000	87.6	3.78	G	3.79	aVQZ
	$^1A'$(V; $\pi \rightarrow \pi^*$)	0.344	91.2	6.69	CCSDT/aVTZ	6.69	aVQZ
	$^1A''$(V; $n \rightarrow \pi^*$)	0.000	79.4	6.72	D	6.74	aVQZ
	$^1A'$(R; $n \rightarrow 3s$)	0.109	89.4	7.08	D	7.12	aVQZ
	$^3A''$(V; $n \rightarrow \pi^*$)		97.0	3.51	H	3.50	aVQZ
	$^3A'$(V; $\pi \rightarrow \pi^*$)		98.6	3.94	D	3.95	aVQZ
	$^3A'$(V; $\pi \rightarrow \pi^*$)		98.4	6.18	D	6.19	aVQZ
	$^3A''$(V; $n \rightarrow \pi^*$)		92.7	6.54	E	6.55	aVQZ
benzene	$^1B_{2u}$(V; $\pi \rightarrow \pi^*$)		86.3	5.06	CCSDT/aVTZ	5.06	aVQZ
	$^1B_{1u}$(V; $\pi \rightarrow \pi^*$)		92.9	6.45	CCSDT/aVTZ	6.44	aVQZ
	$^1E_{1g}$(R; $\pi \rightarrow$ 3s)		92.8	6.52	CCSDT/aVTZ	6.54	aVQZ
	$^1A_{2u}$(R; $\pi \rightarrow$ 3p)	0.066	93.4	7.08	CCSDT/aVTZ	7.10	aVQZ
	$^1E_{2u}$(R; $\pi \rightarrow$ 3p)		92.8	7.15	CCSDT/aVTZ	7.16	aVQZ
	$^3B_{1u}$(V; $\pi \rightarrow \pi^*$)		98.6	4.16	D	4.17	aVQZ
	$^3E_{1u}$(V; $\pi \rightarrow \pi^*$)		97.1	4.85	D	4.86	aVQZ
	$^3B_{2u}$(V; $\pi \rightarrow \pi^*$)		98.1	5.81	D	5.81	aVQZ
butadiene	^1B_u(V; $\pi \rightarrow \pi^*$)	0.664	93.3	6.22	B	6.21	aVQZ
	^1B_g(R; $\pi \rightarrow$ 3s)		94.1	6.33	B	6.35	aVQZ
	^1A_g(V; $\pi \rightarrow \pi^*$)		75.1	6.50	F	6.50	aVQZ
	^1A_u(R; $\pi \rightarrow$ 3p)	0.001	94.1	6.64	B	6.66	aVQZ
	^1A_u(R; $\pi \rightarrow$ 3p)	0.049	94.1	6.80	B	6.82	aVQZ
	^1B_u(R; $\pi \rightarrow$ 3p)	0.055	93.8	7.68	C	7.54	aVQZ
	^3B_u(V; $\pi \rightarrow \pi^*$)		98.4	3.36	D	3.37	aVQZ
	^3A_g(V; $\pi \rightarrow \pi^*$)		98.7	5.20	D	5.21	aVQZ
	^3B_g(R; $\pi \rightarrow$ 3s)		97.9	6.29	D	6.31	aVQZ
cyanoacetylene	$^1\Sigma^-$(V; $\pi \rightarrow \pi^*$)		94.3	5.80	A	5.79	aV5Z
	$^1\Delta$(V; $\pi \rightarrow \pi^*$)		94.0	6.07	A	6.05	aV5Z
	$^3\Sigma^+$(V; $\pi \rightarrow \pi^*$)		98.5	4.44	CCSDT/aVTZ	4.46	aV5Z
	$^3\Delta$(V; $\pi \rightarrow \pi^*$)		98.2	5.21	CCSDT/aVTZ	5.21	aV5Z
	$^1A''$[F] (V; $\pi \rightarrow \pi^*$)	0.004	93.6	3.54	A	3.54	aVQZ
cyanoformaldehyde	$^1A''$(V; $n \rightarrow \pi^*$)	0.001	89.8	3.81	CCSDT/aVTZ	3.82	aVQZ
	$^1A''$(V; $\pi \rightarrow \pi^*$)	0.000	91.9	6.46	CCSDT/aVTZ	6.45	aVQZ
	$^3A''$(V; $n \rightarrow \pi^*$)		97.6	3.44	D	3.45	aVQZ
	$^3A'$(V; $\pi \rightarrow \pi^*$)		98.4	5.01	D	5.02	aVQZ
cyanogen	$^1\Sigma_u^-$(V; $\pi \rightarrow \pi^*$)		94.1	6.39	A	6.38	aV5Z
	$^1\Delta_u$(V; $\pi \rightarrow \pi^*$)		93.4	6.66	A	6.64	aV5Z
	$^3\Sigma_u^+$(V; $\pi \rightarrow \pi^*$)		98.5	4.91	B	4.93	aV5Z
	$^1\Sigma_u^-$[F] (V; $\pi \rightarrow \pi^*$)		93.4	5.05	A	5.03	aV5Z
cyclopentadiene	$^1B_2$(V; $\pi \rightarrow \pi^*$)	0.084	93.8	5.56	CCSDT/aVTZ	5.55	aVQZ
	$^1A_2$(R; $\pi \rightarrow 3s$)		94.0	5.78	CCSDT/aVTZ	5.80	aVQZ
	$^1B_1$(R; $\pi \rightarrow 3p$)	0.037	94.2	6.41	CCSDT/aVTZ	6.42	aVQZ
	$^1A_2$(R; $\pi \rightarrow 3p$)		93.8	6.46	CCSDT/aVTZ	6.47	aVQZ
	$^1B_2$(R; $\pi \rightarrow 3p$)	0.046	94.2	6.56	CCSDT/aVTZ	6.55	aVQZ
	$^1A_1$(V; $\pi \rightarrow \pi^*$)	0.001	78.9	6.52	CCSDT/aVTZ	6.52	aVQZ
	$^3B_2$(V; $\pi \rightarrow \pi^*$)		98.4	3.31	D	3.31	aVQZ
	$^3A_1$(V; $\pi \rightarrow \pi^*$)		98.6	5.11	D	5.12	aVQZ
	$^3A_2$(R; $\pi \rightarrow 3s$)		97.9	5.73	D	5.75	aVQZ
	$^3B_1$(R; $\pi \rightarrow 3p$)		97.9	6.36	D	6.38	aVQZ

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Table 11. continued

				TBE/aVTZ		TBE/CBS	
	state	f	$\%T_1$	value	protocol[b]	value	corr.
cyclopropenone	$^1B_1$(V; $n \rightarrow \pi^*$)	0.000	87.7	4.26	B	4.28	aV5Z
	$^1A_2$(V; $n \rightarrow \pi^*$)		91.0	5.55	B	5.56	aV5Z
	$^1B_2$(R; $n \rightarrow 3s$)	0.003	90.8	6.34	B	6.40	aV5Z
	$^1B_2$(V; $\pi \rightarrow \pi^*$)	0.047	86.5	6.54	B	6.56	aV5Z
	$^1B_2$(R; $n \rightarrow 3p$)	0.018	91.1	6.98	B	7.01	aV5Z
	$^1A_1$(R; $n \rightarrow 3p$)	0.003	91.2	7.02	B	7.08	aV5Z
	$^1A_1$(V; $\pi \rightarrow \pi^*$)	0.320	90.8	8.28	B	8.26	aV5Z
	$^3B_1$(V; $n \rightarrow \pi^*$)		96.0	3.93	CCSDT/aVTZ	3.96	aV5Z
	$^3B_2$(V; $\pi \rightarrow \pi^*$)		97.9	4.88	CCSDT/aVTZ	4.91	aV5Z
	$^3A_2$(V; $n \rightarrow \pi^*$)		97.5	5.35	CCSDT/aVTZ	5.37	aV5Z
	$^3A_1$(V; $\pi \rightarrow \pi^*$)		98.1	6.79	CCSDT/aVTZ	6.81	aV5Z
cyclopropenethione	$^1A_2$(V; $n \rightarrow \pi^*$)		89.6	3.41	B	3.41	aV5Z
	$^1B_1$(V; $n \rightarrow \pi^*$)	0.000	84.8	3.45	B	3.48	aV5Z
	$^1B_2$(V; $\pi \rightarrow \pi^*$)	0.007	83.0	4.60	B	4.62	aV5Z
	$^1B_2$(R; $n \rightarrow 3s$)	0.048	91.8	5.34	B	5.40	aV5Z
	$^1A_1$(V; $\pi \rightarrow \pi^*$)	0.228	89.0	5.46	B	5.46	aV5Z
	$^1B_2$(R; $n \rightarrow 3p$)	0.084	91.3	5.92	B	5.94	aV5Z
	$^3A_2$(V; $n \rightarrow \pi^*$)		97.2	3.28	D	3.28	aV5Z
	$^3B_1$(V; $n \rightarrow \pi^*$)		94.5	3.32	CCSDT/aVTZ	3.36	aV5Z
	$^3B_2$(V; $\pi \rightarrow \pi^*$)		96.5	4.01	D	4.04	aV5Z
	$^3A_1$(V; $\pi \rightarrow \pi^*$)		98.2	4.01	D	4.01	aV5Z
diacetylene	$^1\Sigma_u^-$(V; $\pi \rightarrow \pi^*$)		94.4	5.33	A	5.32	aV5Z
	$^1\Delta_u$ (V; $\pi \rightarrow \pi^*$)		94.1	5.61	A	5.60	aV5Z
	$^3\Sigma_u^+$(V; $\pi \rightarrow \pi^*$)		98.5	4.10	C	4.13	aV5Z
	$^3\Delta_u$ (V; $\pi \rightarrow \pi^*$)		98.2	4.78	B	4.78	aV5Z
furan	$^1A_2$(R; $\pi \rightarrow 3s$)		93.8	6.09	CCSDT/aVTZ	6.11	aVQZ
	$^1B_2$(V; $\pi \rightarrow \pi^*$)	0.163	93.0	6.37	CCSDT/aVTZ	6.37	aVQZ
	$^1A_1$(V; $\pi \rightarrow \pi^*$)	0.000	92.4	6.56	CCSDT/aVTZ	6.56	aVQZ
	$^1B_1$(R; $\pi \rightarrow 3p$)	0.038	93.9	6.64	CCSDT/aVTZ	6.66	aVQZ
	$^1A_2$(R; $\pi \rightarrow 3p$)		93.6	6.81	CCSDT/aVTZ	6.83	aVQZ
	$^1B_2$(R; $\pi \rightarrow 3p$)	0.008	93.5	7.24	D	7.14	aVQZ
	$^3B_2$(V; $\pi \rightarrow \pi^*$)		98.4	4.20	D	4.20	aVQZ
	$^3A_1$(V; $\pi \rightarrow \pi^*$)		98.1	5.46	D	5.47	aVQZ
	$^3A_2$(R; $\pi \rightarrow 3s$)		97.9	6.02	D	6.05	aVQZ
	$^3B_1$(R; $\pi \rightarrow 3p$)		97.9	6.59	D	6.61	aVQZ
glyoxal	^1A_u(V; $n \rightarrow \pi^*$)	0.000	91.0	2.88	B	2.88	aV5Z
	^1B_g(V; $n \rightarrow \pi^*$)		88.3	4.24	B	4.25	aV5Z
	^1A_g(V; n, n $\rightarrow \pi^*,\pi^*$)		0.5	5.61	F	5.60	aV5Z
	^1B_g(V; $n \rightarrow \pi^*$)		83.9	6.57	B	6.58	aV5Z
	^1B_u(R; $n \rightarrow 3p$)	0.095	91.7	7.71	B	7.78	aV5Z
	^3A_u(V; $n \rightarrow \pi^*$)		97.6	2.49	CCSDT/aVTZ	2.50	aV5Z
	^3B_g(V; $n \rightarrow \pi^*$)		97.4	3.89	CCSDT/aVTZ	3.91	aV5Z
	^3B_u(V; $\pi \rightarrow \pi^*$)		98.5	5.15	CCSDT/aVTZ	5.17	aV5Z
	^3A_g(V; $\pi \rightarrow \pi^*$)		98.8	6.30	CCSDT/aVTZ	6.31	aV5Z
imidazole	$^1A''$(R; $\pi \rightarrow 3s$)	0.001	93.0	5.71	D	5.73	aVQZ
	$^1A'$(V; $\pi \rightarrow \pi^*$)	0.124	89.6	6.41	D	6.41	aVQZ
	$^1A''$(V; $n \rightarrow \pi^*$)	0.028	93.6	6.50	D	6.53	aVQZ
	$^1A'$(R; $\pi \rightarrow 3p$)	0.035	88.9	6.83	D	6.82	aVQZ
	$^3A'$(V; $\pi \rightarrow \pi^*$)		98.3	4.73	E	4.74	aVQZ
	$^3A''$(R; $\pi \rightarrow 3s$)		97.6	5.66	D	5.69	aVQZ
	$^3A'$(V; $\pi \rightarrow \pi^*$)		97.9	5.74	E	5.75	aVQZ
	$^3A''$(V; $n \rightarrow \pi^*$)		97.3	6.31	D	6.31	aVQZ
isobutene	$^1B_1$(R; $\pi \rightarrow 3s$)	0.006	94.1	6.46	CCSDT/aVTZ	6.48	aVQZ
	$^1A_1$(R; $\pi \rightarrow 3p$)	0.228	94.2	7.01	CCSDT/aVTZ	7.00	aVQZ
	$^3A_1$(V; ($\pi \rightarrow \pi^*$)		98.9	4.53	D	4.54	aVQZ
methylenecyclopropene	$^1B_2$(V; $\pi \rightarrow \pi^*$)	0.011	85.4	4.28	B	4.29	aV5Z

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Table 11. continued

				TBE/aVTZ		TBE/CBS	
	state	f	$\%T_1$	value	protocol[b]	value	corr.
	$^1B_1$(R; $\pi \rightarrow 3s$)	0.005	93.6	5.44	B	5.47	aV5Z
	$^1A_2$(R; $\pi \rightarrow 3p$)		93.3	5.96	B	5.98	aV5Z
	$^1A_1$(V; $\pi \rightarrow \pi^*$)	0.224	92.8	*6.12*	B	*6.03*	aV5Z
	$^3B_2$(V; $\pi \rightarrow \pi^*$)		97.2	3.49	CCSDT/aVTZ	3.50	aV5Z
	$^3A_1$(V; $\pi \rightarrow \pi^*$)		98.6	4.74	D	4.75	aV5Z
propynal	$^1A''$(V; $n \rightarrow \pi^*$)	0.000	89.0	3.80	CCSDT/aVTZ	3.81	aVQZ
	$^1A''$(V; $\pi \rightarrow \pi^*$)	0.000	92.9	5.54	CCSDT/aVTZ	5.53	aVQZ
	$^3A''$(V; $n \rightarrow \pi^*$)		97.4	3.47	D	3.48	aVQZ
	$^3A'$(V; $\pi \rightarrow \pi^*$)		98.3	4.47	D	4.48	aVQZ
pyrazine	$^1B_{3u}$(V; $n \rightarrow \pi^*$)	0.006	90.1	4.15	CCSDT/aVTZ	4.15	aVQZ
	^1A_u(V; $n \rightarrow \pi^*$)		88.6	4.98	CCSDT/aVTZ	4.99	aVQZ
	$^1B_{2u}$(V; $\pi \rightarrow \pi^*$)	0.078	86.9	5.02	CCSDT/aVTZ	5.01	aVQZ
	$^1B_{2g}$(V; $n \rightarrow \pi^*$)		85.6	5.71	CCSDT/aVTZ	5.71	aVQZ
	^1A_g(R; $n \rightarrow 3s$)		91.1	6.65	CCSDT/aVTZ	6.69	aVQZ
	$^1B_{1g}$(V; $n \rightarrow \pi^*$)		84.2	6.74	CCSDT/aVTZ	6.74	aVQZ
	$^1B_{1u}$(V; $\pi \rightarrow \pi^*$)	0.063	92.8	6.88	CCSDT/aVTZ	6.87	aVQZ
	$^1B_{1g}$(R; $\pi \rightarrow 3s$)		93.8	7.21	CCSDT/aVTZ	7.24	aVQZ
	$^1B_{2u}$(R; $n \rightarrow 3p$)	0.037	90.8	7.24	D	7.28	aVQZ
	$^1B_{1u}$(R; $n \rightarrow 3p$)	0.128	91.4	7.44	D	7.47	aVQZ
	$^1B_{1u}$(V; $\pi \rightarrow \pi^*$)	0.285	90.5	*7.98*	D	*7.97*	aVQZ
	$^3B_{3u}$(V; $n \rightarrow \pi^*$)		97.3	3.59	D	3.59	aVQZ
	$^3B_{1u}$(V; $\pi \rightarrow \pi^*$)		98.5	4.35	D	4.36	aVQZ
	$^3B_{2u}$(V; ($\pi \rightarrow \pi^*$)		97.6	4.39	D	4.39	aVQZ
	^3A_u(V; $n \rightarrow \pi^*$)		96.1	4.93	D	4.94	aVQZ
	$^3B_{2g}$(V; $n \rightarrow \pi^*$)		97.0	5.08	D	5.09	aVQZ
	$^3B_{1u}$(V; $\pi \rightarrow \pi^*$)		97.0	5.28	D	5.28	aVQZ
pyridazine	$^1B_1$(V; $n \rightarrow \pi^*$)	0.005	89.0	3.83	D	3.83	aVQZ
	$^1A_2$(V; $n \rightarrow \pi^*$)		86.9	4.37	D	4.38	aVQZ
	$^1A_1$(V; $\pi \rightarrow \pi^*$)	0.016	85.8	5.26	D	5.26	aVQZ
	$^1A_2$(V; $n \rightarrow \pi^*$)		86.2	5.72	D	5.72	aVQZ
	$^1B_2$(R; $n \rightarrow 3s$)	0.001	88.5	6.17	D	6.21	aVQZ
	$^1B_1$(V; $n \rightarrow \pi^*$)	0.004	87.0	6.37	D	6.37	aVQZ
	$^1B_2$(V; $\pi \rightarrow \pi^*$)	0.010	90.6	6.75	D	6.74	aVQZ
	$^3B_1$(V; $n \rightarrow \pi^*$)		97.1	3.19	D	3.20	aVQZ
	$^3A_2$(V; $n \rightarrow \pi^*$)		96.2	4.11	D	4.12	aVQZ
	$^3B_2$(V; $\pi \rightarrow \pi^*$)		98.5	*4.34*	D	*4.35*	aVQZ
	$^3A_1$(V; $\pi \rightarrow \pi^*$)		97.3	4.82	D	4.81	aVQZ
pyridine	$^1B_1$(V; $n \rightarrow \pi^*$)	0.004	88.4	4.95	D	4.95	aVQZ
	$^1B_2$(V; $\pi \rightarrow \pi^*$)	0.028	86.5	5.14	D	5.14	aVQZ
	$^1A_2$(V; $n \rightarrow \pi^*$)		87.9	5.40	D	5.41	aVQZ
	$^1A_1$(V; $\pi \rightarrow \pi^*$)	0.010	92.1	6.62	D	6.61	aVQZ
	$^1A_1$(R; $n \rightarrow 3s$)	0.011	89.7	6.76	D	6.80	aVQZ
	$^1A_2$(R; $\pi \rightarrow 3s$)		93.2	6.82	D	6.84	aVQZ
	$^1B_2$(V; $\pi \rightarrow \pi^*$)	0.319	90.0	*7.40*	D	*7.42*	aVQZ
	$^1B_1$(R; $\pi \rightarrow 3p$)	0.045	93.6	7.38	D	7.40	aVQZ
	$^1A_1$(V; $\pi \rightarrow \pi^*$)	0.291	90.5	7.39	D	7.40	aVQZ
	$^3A_1$(V; $\pi \rightarrow \pi^*$)		98.5	4.30	D	4.31	aVQZ
	$^3B_1$(V; $n \rightarrow \pi^*$)		97.0	4.46	D	4.47	aVQZ
	$^3B_2$(V; $\pi \rightarrow \pi^*$)		97.3	4.79	D	4.79	aVQZ
	$^3A_1$(V; $\pi \rightarrow \pi^*$)		97.1	5.04	E	5.04	aVQZ
	$^3A_2$(V; $n \rightarrow \pi^*$)		95.8	5.36	D	5.38	aVQZ
	$^3B_2$(V; $\pi \rightarrow \pi^*$)		97.7	6.24	D	6.24	aVQZ
pyrimidine	$^1B_1$(V; $n \rightarrow \pi^*$)	0.005	88.6	4.44	D	4.45	aVQZ
	$^1A_2$(V; $n \rightarrow \pi^*$)		88.5	4.85	D	4.86	aVQZ
	$^1B_2$(V; $\pi \rightarrow \pi^*$)	0.028	86.3	5.38	D	5.37	aVQZ
	$^1A_2$(V; $n \rightarrow \pi^*$)		86.7	5.92	D	5.92	aVQZ

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Table 11. continued

				TBE/aVTZ		TBE/CBS	
	state	f	$\%T_1$	value	protocol[b]	value	corr.
	$^1B_1$(V; $n \rightarrow \pi^*$)	0.005	86.7	6.26	D	6.27	aVQZ
	$^1B_2$(R; $n \rightarrow 3s$)	0.005	90.3	6.70	D	6.74	aVQZ
	$^1A_1$(V; $\pi \rightarrow \pi^*$)	0.036	91.5	6.88	D	6.87	aVQZ
	$^3B_1$(V; $n \rightarrow \pi^*$)		96.8	4.09	D	4.10	aVQZ
	$^3A_1$(V; $\pi \rightarrow \pi^*$)		98.3	*4.51*	D	*4.52*	aVQZ
	$^3A_2$(V; $n \rightarrow \pi^*$)		96.5	4.66	D	4.67	aVQZ
	$^3B_2$(V; $\pi \rightarrow \pi^*$)		97.4	4.96	D	4.96	aVQZ
pyrrole	$^1A_2$(R; $\pi \rightarrow 3s$)		92.9	5.24	CCSDT/aVTZ	5.27	aVQZ
	$^1B_1$(R; $\pi \rightarrow 3p$)	0.015	92.4	6.00	CCSDT/aVTZ	6.03	aVQZ
	$^1A_2$(R; $\pi \rightarrow 3p$)		93.0	6.00	D	6.02	aVQZ
	$^1B_2$(V; ($\pi \rightarrow \pi^*$)	0.164	92.5	6.26	CCSDT/aVTZ	6.23	aVQZ
	$^1A_1$(V; $\pi \rightarrow \pi^*$)	0.001	86.3	6.30	CCSDT/aVTZ	6.29	aVQZ
	$^1B_2$(R; $\pi \rightarrow 3p$)	0.003	92.6	6.83	D	6.74	aVQZ
	$^3B_2$(V; $\pi \rightarrow \pi^*$)		98.3	4.51	D	4.51	aVQZ
	$^3A_2$(R; $\pi \rightarrow 3s$)		97.6	5.21	D	5.24	aVQZ
	$^3A_1$(V; $\pi \rightarrow \pi^*$)		97.8	5.45	D	5.46	aVQZ
	$^3B_1$(R; $\pi \rightarrow 3p$)		97.4	5.91	D	5.94	aVQZ
tetrazine	$^1B_{3u}$(V; $n \rightarrow \pi^*$)	0.006	89.8	2.47	CCSDT/aVTZ	2.46	aVQZ
	^1A_u(V; $n \rightarrow \pi^*$)		87.9	3.69	CCSDT/aVTZ	3.70	aVQZ
	^1A_g(V; n, n $\rightarrow \pi^*, \pi^*$)		0.7	*4.61*	NEVPT2/aVTZ	*4.59*	aVQZ
	$^1B_{1g}$(V; $n \rightarrow \pi^*$)		83.1	4.93	CCSDT/aVTZ	4.92	aVQZ
	$^1B_{2u}$(V; $\pi \rightarrow \pi^*$)	0.055	85.4	5.21	CCSDT/aVTZ	5.20	aVQZ
	$^1B_{2g}$(V; $n \rightarrow \pi^*$)		81.7	5.45	CCSDT/aVTZ	5.45	aVQZ
	^1A_u(V; $n \rightarrow \pi^*$)		87.7	5.53	CCSDT/aVTZ	5.53	aVQZ
	$^1B_{3g}$(V; n, n $\rightarrow \pi^*, \pi^*$)		0.7	*6.15*	NEVPT2/aVTZ	*6.13*	aVQZ
	$^1B_{2g}$(V; $n \rightarrow \pi^*$)		80.2	6.12	D	6.12	aVQZ
	$^1B_{1g}$(V; $n \rightarrow \pi^*$)		85.1	6.91	D	6.91	aVQZ
	$^3B_{3u}$(V; $n \rightarrow \pi^*$)		97.1	1.85	D	1.86	aVQZ
	^3A_u(V; $n \rightarrow \pi^*$)		96.3	3.45	D	3.46	aVQZ
	$^3B_{1g}$(V; $n \rightarrow \pi^*$)		97.0	4.20	D	4.21	aVQZ
	$^3B_{1u}$(V; $\pi \rightarrow \pi^*$)		98.5	*4.49*	D	*4.49*	aVQZ
	$^3B_{2u}$(V; $\pi \rightarrow \pi^*$)		97.5	4.52	D	4.52	aVQZ
	$^3B_{2g}$(V; $n \rightarrow \pi^*$)		96.4	5.04	D	5.04	aVQZ
	^3A_u(V; $n \rightarrow \pi^*$)		96.6	5.11	D	5.11	aVQZ
	$^3B_{3g}$(V; n, n $\rightarrow \pi^*, \pi^*$)		5.7	*5.51*	NEVPT2/aVTZ	*5.50*	aVQZ
	$^3B_{1u}$(V; $\pi \rightarrow \pi^*$)		96.6	5.42	D	5.43	aVQZ
thioacetone	$^1A_2$(V; $n \rightarrow \pi^*$)		88.9	2.53	B	2.54	aVQZ
	$^1B_2$(R; $n \rightarrow 4s$)	0.052	91.3	5.56	B	5.61	aVQZ
	$^1A_1$(V; $\pi \rightarrow \pi^*$)	0.242	90.6	5.88	B	5.86	aVQZ
	$^1B_2$(R; $n \rightarrow 4p$)	0.028	92.4	6.51	C	6.52	aVQZ
	$^1A_1$(R; $n \rightarrow 4p$)	0.023	91.6	6.61	B	6.64	aVQZ
	$^3A_2$(V; $n \rightarrow \pi^*$)		97.4	2.33	D	2.34	aVQZ
	$^3A_1$(V; $\pi \rightarrow \pi^*$)		98.7	3.45	D	3.46	aVQZ
thiophene	$^1A_1$(V; $\pi \rightarrow \pi^*$)	0.070	87.6	5.64	CCSDT/aVTZ	5.63	aVQZ
	$^1B_2$(V; $\pi \rightarrow \pi^*$)	0.079	91.5	5.98	CCSDT/aVTZ	5.96	aVQZ
	$^1A_2$(R; $\pi \rightarrow 3s$)		92.6	6.14	CCSDT/aVTZ	6.16	aVQZ
	$^1B_1$(R; $\pi \rightarrow 3p$)	0.010	90.1	6.14	CCSDT/aVTZ	6.11	aVQZ
	$^1A_2$(R; $\pi \rightarrow 3p$)		91.8	6.21	CCSDT/aVTZ	6.18	aVQZ
	$^1B_1$(R; $\pi \rightarrow 3s$)	0.000	92.8	6.49	CCSDT/aVTZ	6.52	aVQZ
	$^1B_2$(R; $\pi \rightarrow 3p$)	0.082	92.4	7.29	CCSDT/aVTZ	7.18	aVQZ
	$^1A_1$(V; $\pi \rightarrow \pi^*$)	0.314	86.5	*7.31*	E	*7.29*	aVQZ
	$^3B_2$(V; $\pi \rightarrow \pi^*$)		98.2	3.92	D	3.91	aVQZ
	$^3A_1$(V; $\pi \rightarrow \pi^*$)		97.7	4.76	D	4.76	aVQZ
	$^3B_1$(R;$\pi \rightarrow 3p$)		96.6	5.93	D	5.90	aVQZ
	$^3A_2$(R; $\pi \rightarrow 3s$)		97.5	6.08	D	5.98	aVQZ
thiopropynal	$^1A''$(V; $n \rightarrow \pi^*$)	0.000	87.5	2.03	CCSDT/aVTZ	2.04	aVQZ

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Table 11. continued

	state	f	$\%T_1$	TBE/aVTZ value	TBE/aVTZ protocol[b]	TBE/CBS value	TBE/CBS corr.
	$^3A''(V; n \rightarrow \pi^*)$		97.2	1.80	D	1.81	aVQZ
triazine	$^1A_1''(V; n \rightarrow \pi^*)$		88.3	4.72	CCSDT/aVTZ	4.72	aVQZ
	$^1A_2''(V; n \rightarrow \pi^*)$	0.014	88.3	4.75	CCSDT/aVTZ	4.74	aVQZ
	$^1E''(V; n \rightarrow \pi^*)$		88.3	4.78	CCSDT/aVTZ	4.78	aVQZ
	$^1A_2'(V; \pi \rightarrow \pi^*)$		85.7	5.75	CCSDT/aVTZ	5.75	aVQZ
	$^1A_1'(V; \pi \rightarrow \pi^*)$		90.4	7.24	CCSDT/aVTZ	7.23	aVQZ
	$^1E'(R; n \rightarrow 3s)$	0.016	90.9	7.32	CCSDT/aVTZ	7.36	aVQZ
	$^1E''(V; n \rightarrow \pi^*)$		82.6	7.78	CCSDT/aVTZ	7.76	aVQZ
	$^1E'(V; \pi \rightarrow \pi^*)$	0.451	90.0	7.94	CCSDT/aVTZ	7.93	aVQZ
	$^3A_2''(V; n \rightarrow \pi^*)$		96.7	4.33	D	4.34	aVQZ
	$^3E''(V; n \rightarrow \pi^*)$		96.6	4.51	D	4.51	aVQZ
	$^3A_1''(V; n \rightarrow \pi^*)$		96.2	4.73	D	4.74	aVQZ
	$^3A_1'(V; \pi \rightarrow \pi^*)$		98.2	4.85	D	4.86	aVQZ
	$^3E'(V; \pi \rightarrow \pi^*)$		96.9	5.59	E	5.59	aVQZ
	$^3A_2'(V; (\pi \rightarrow \pi^*)$		97.6	6.62	D	6.61	aVQZ

[a]The composite protocol to generate these TBEs is also reported (see footnote *b*). In the right-most column, we list the TBE values obtained by including an additional correction (obtained at the CC3 level) for the basis set incompleteness error. Values displayed in italics are likely to be relatively less accurate. All values are obtained in the frozen-core approximation. [b]Protocol A: CCSDT/aVTZ value corrected by the difference between CCSDTQ/aVDZ and CCSDT/aVDZ. Protocol B: CCSDT/aVTZ value corrected by the difference between CCSDTQ/6-31+G(d) and CCSDT/6-31+G(d). Protocol C: CC3/aVTZ value corrected by the difference between CCSDTQ/6-31+G(d) and CC3/6-31+G(d). Protocol D: CC3/aVTZ value corrected by the difference between CCSDT/aVDZ and CC3/aVDZ. Protocol E: CC3/aVTZ value corrected by the difference between CCSDT/6-31+G(d) and CC3/6-31+G(d). Protocol F: FCI/aVDZ value (from ref 72) corrected by the difference between CCSDT/aVTZ and CCSDT/aVDZ. Protocol G: FCI/6-31+G(d) value corrected by the difference between CCSDT/aVTZ and CCSDT/6-31+G(d). Protocol H: FCI/6-31+G(d) value corrected by the difference between CC3/aVTZ and CC3/6-31+G(d).

with a nearby Rydberg transition that is separated by only 0.03 eV at the CC3/aVTZ level. This obviously makes the analysis particularly challenging for this specific transition.

The results obtained for both pyrimidine and triazine are listed in Tables 10 and S10. Because the former derivative can be viewed as the smallest model of DNA bases, previous theoretical[23,25−27,30,66,69,160,183,212,213,218,249−251] and experimental[234,252,253] studies are rather extensive. For triazine, which belongs to a nonabelian point group, theoretical studies are scarcer,[23,25−27,30,66,69,212,213,244,254,255] especially for the triplets,[244,254,255] whereas the experimental data are also limited.[234,244] As in pyridazine and pyridine, all the ESs listed in Table 10 show $\%T_1$ values larger than 85% for singlets and 95% for triplets, so that CC3 and CCSDT are highly coherent, except maybe for the $^3A_1(\pi \rightarrow \pi^*)$ transitions in pyrimidine. The basis set effects are also small, with no variation larger than 0.10 (0.03) eV between double- and triple-ζ (triple- and quadruple-ζ) for valence transitions and only slightly larger variations for the two Rydberg transitions (+0.04 eV between aVTZ and aVQZ). For both compounds, the current values are almost systematically larger than previously published data, with our CC3 values being typically bracketed by the published CASPT2 and the present NEVPT2 estimates. For the triplets of triazine, the three lowest ESs previously estimated by CASPT2[255] are too low by roughly half an electronvolt.

4. THEORETICAL BEST ESTIMATES

Table 11 reports our two sets of TBEs: a set obtained with the aVTZ basis set and one set including an additional correction for the one-electron basis set incompleteness error. The details of our protocol employed to generate these TBEs are also provided in Table 11. For all states with a dominant single-excitation character (that is when $\%T_1 > 80\%$), we rely on CC results using an incremental strategy to generate these TBEs. As explained in the footnotes of Table 11, this means that we add the basis set correction (i.e., the excitation energy difference between two calculations performed with a large and a small basis set) obtained with a "lower" level of theory, e.g., CC3, to correct the result obtained at a "higher" level of theory, e.g., CCSDTQ, but with the smaller basis set. In our previous contribution,[28] we have extensively tested this protocol for small compounds for which CCSDTQ/aVTZ calculations were achievable. It turned out that correcting CCSDTQ/6-31+G(d) with the CC3 or CCSDT basis set effect was very effective with a MAE of 0.01 eV as compared to the true value. There are only two exceptions for which we eschew using this CC incremental strategy: two ESs in acrolein for which nicely converged FCI values indicated non-negligible CCSDT errors. For ES with $\%T_1$ values between 70% and 80%, our previous works indicated that CCSDT tends to overshoot the transition energies by roughly 0.05−0.10 eV and that NEVPT2 errors tend to be, on average, slightly larger.[72] Therefore, if CCSDTQ or FCI results are not available, it is extremely difficult to make the final call. For the other transitions, we relied either on the current or previous FCI data or the NEVPT2 values as reference. The italicized transition energies in Table 11 are believed to be (relatively) less accurate. This is the case when (i) the NEVPT2 result has to be selected; (ii) the CC calculations yield quite large changes in excitation energies while incrementing the excitation order despite large $\%T_1$; and (iii) there is a very strong ES mixing making hard to follow a specific transition from one method (or one basis) to another.

To determine the basis set corrections beyond augmented triple-ζ, we use the CC3/aVQZ or CC3/aV5Z results. For several compounds, we also provide in the SI CC3/d-aVQZ transition energies (i.e., with an additional set of diffuse functions). However, we do not consider such values as reference because the addition of a second set of diffuse orbitals

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Table 12. Mean Signed Error (MSE), Mean Absolute Error (MAE), Root-Mean-Square Error (RMSE), Standard Deviation of the Errors (SDE), as Well as the Maximum Positive [Max(+)] and Negative [Max(−)] Errors with Respect to the TBE/aVTZ Reported in Table 11[a]

method	count	MSE	MAE	RMSE	SDE	Max(+)	Max(−)
CIS(D)	221	0.16	0.23	0.29	0.24	0.96	−0.69
ADC(2)	218	0.01	0.14	0.20	0.19	0.64	−0.73
CC2	223	0.03	0.15	0.21	0.20	0.59	−0.68
STEOM-CCSD	190	0.01	0.12	0.15	0.14	0.59	−0.42
CCSD	223	0.11	0.13	0.16	0.12	0.62	−0.16
CCSDR(3)	134	0.05	0.05	0.07	0.05	0.36	−0.03
CCSDT-3	127	0.05	0.05	0.07	0.04	0.26	0.00
CC3	223	0.00	0.01	0.02	0.02	0.17	−0.05
NEVPT2	223	0.09	0.13	0.17	0.14	0.46	−0.42

[a]All these statistical quantities are reported in eV and have been obtained with the aVTZ basis set. "Count" refers to the number of states.

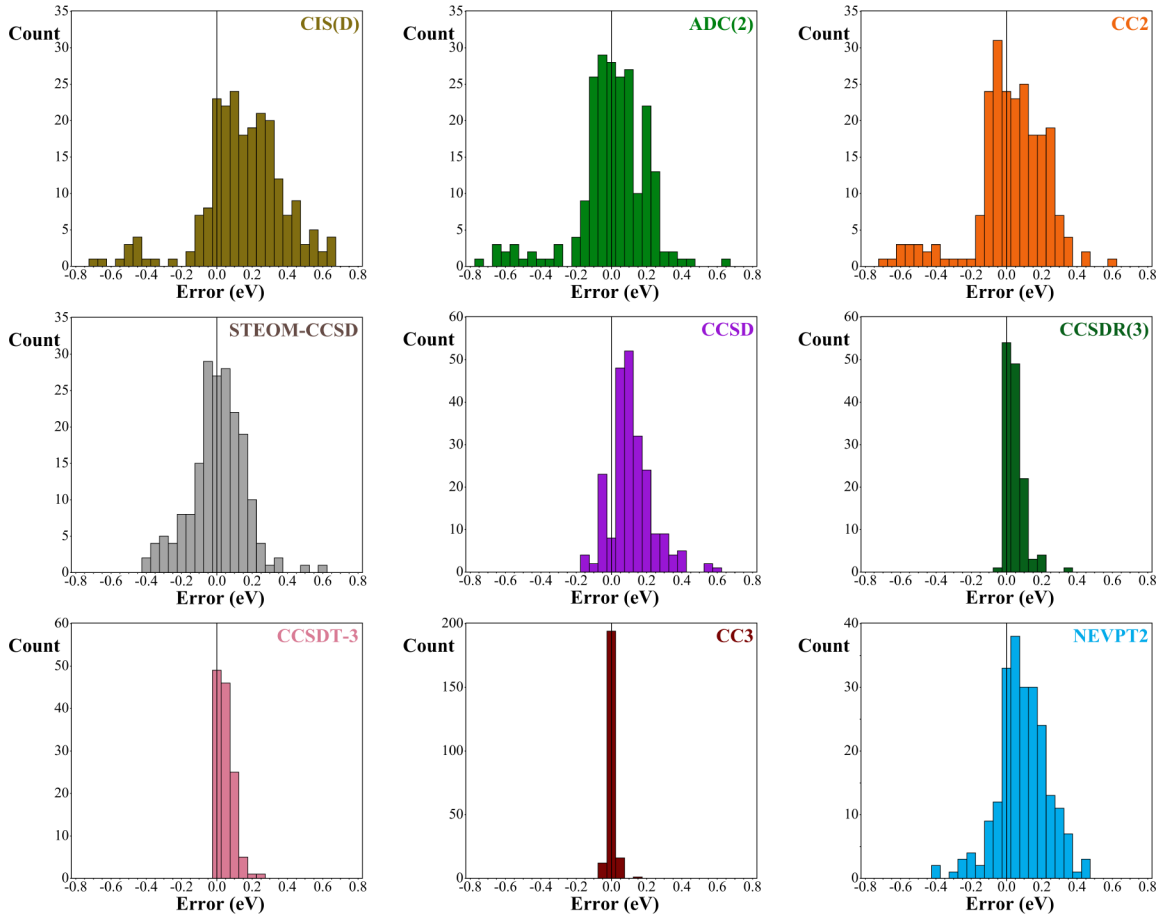

Figure 1. Histograms of the error distribution obtained with various levels of theory, taking the TBE/aVTZ of Table 11 as references. Note the differences in scaling in the vertical axes.

only significantly modifies the transition energies when they also induce a stronger ES mixing. We also stick to the frozen-core approximation for two reasons: (i) the effect of correlating the core electrons is generally negligible (typically ±0.02 eV) for the compounds under study (see the SI for examples), and (ii) it would be, in principle, necessary to add core polarization functions in such a case, which would have been technically difficult for most of the compounds considered here.

Table 11 encompasses 238 ESs, each of them obtained, at least, at the CCSDT level. This set can be decomposed as follows: 144 singlet and 94 triplet transitions, or 174 valence (99 $\pi \rightarrow \pi^*$, 71 $n \rightarrow \pi^*$, and 4 double excitations) and 64 Rydberg transitions. Among these transition energies, 14 can be considered as "unsafe" and are reported in italics accordingly. This definitely corresponds to a very significant extension of our previous ES data sets (see Introduction). Taken all together, they offer a consistent, diverse, and accurate ensemble of transition energies for approximately 350 electronic transitions of various natures in small and medium-sized organic molecules. Table 11 also reports 90 oscillator strengths, *f*, which makes it, to the best of our knowledge, the largest set of CC3/aVTZ oscillator strengths reported to date, the previous effort being mostly performed at the CC3/TZVP level for Thiel's set.[69] It should also be pointed out that all these data are obtained on

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CC3/aVTZ geometries, consistently with our previous works.[28,72]

5. BENCHMARKS

Having at hand such a large set of accurate transition energies, it seems natural to pursue previous benchmarking efforts. More specifically, we assess here the performance of eight popular wave function approaches, namely, CIS(D), ADC(2), CC2, STEOM-CCSD, CCSD, CCSDR(3), CCSDT-3, and CC3. The complete list of results can be found in Table S40 of the SI. To identify the ESs for all approaches, we have made, as for the TBE above, choices based on the usual criteria (symmetry, oscillator strength, ordering, and nature of the involved orbitals). Except for a few cases (see above), assignments are unambiguous. In addition, because all tested approaches are single-reference methods, we have removed from the reference set the "unsafe" transition energies (in italics in Table 11), as well as the four transitions with a dominant double excitation character (with $\%T_1 < 50\%$ as listed in Table 12). For the latter transitions, only CCSDT-3 and CC3 are able to detect their presence but with, of course, extremely large errors. A comprehensive list of results are collected in Table 12 which, more specifically, gathers the MSE, MAE, RMSE, SDE, Max(+), and Max(−). As benchmarks of the NEVPT2 method are quite rare, we have also considered the above-listed NEVPT2 values in our method evaluation. Of course, the results of such multiconfigurational approaches significantly depend on the active space, but our main purpose is to know what typical error one can expect with such a model when reasonable, yet "chemically meaningful" active spaces are considered. Figure 1 shows histograms of the error distributions for these nine methods. Before discussing these, let us stress two obvious biases of this molecular set: (i) it encompasses only conjugated organic molecules containing 4 to 6 non-hydrogen atoms, and (ii) we mainly used CCSDTQ (4 atoms) or CCSDT (5−6 atoms) reference values. As discussed in Section 3.1.5 and in our previous work,[28] the MAEs obtained with these two methods are of the order of 0.01 and 0.03 eV, respectively. This means that any statistical quantity smaller than ∼0.02−0.03 eV is very likely to be irrelevant.

Let us analyze the global performance of all these methods, starting with the most accurate and computationally demanding single-reference models. The relative accuracy of CC3 and CCSDT-3 as compared to CCSDT remains an open question in the literature.[56,71] Indeed, to the best of our knowledge, the only two previous studies discussing this specific aspect are limited to very small compounds.[28,70] According to the results gathered in Table 12, it appears that CC3 has a slight edge over CCSDT-3, although CCSDT-3 is closer to CCSDT in terms of formalism. Indeed, CCSDT-3 seems to provide slightly too large transition energies (MSE of +0.05 eV). These conclusions are qualitatively consistent with the analyses performed on smaller derivatives,[28,70] but the amplitude of the CCSDT-3 deviations is larger in the present set. Although the performance of CC3 might be unduly inflated by the use of CCSDT and CCSDTQ reference values, it is also clear that CC3 very rarely fails (Figure 1). Consequently, CC3 transition energies can be viewed as extremely solid references for any transition with a dominant single-excitation character. This conclusion is again consistent with previous analyses performed on smaller compounds,[28,70,148] as well as with recent comparisons between theoretical and experimental 0-0 energies performed by some of us on medium-sized molecules.[116,117,173] To state it more boldly: it appears likely that CC3 is even more accurate than previously thought. In addition, thanks to the exhaustive and detailed comparisons made in the present work, we can safely conclude that CC3 regularly outperforms CASPT2 and NEVPT2, even when these methods are combined with relatively large active spaces. This statement seems to hold as long as the considered ES does not show a strong multiple excitation character, that is, when $\%T_1 > 70\%$.

The perturbative inclusion of triples as in CCSDR(3) yields a very small MAE (0.05 eV) for a much lighter computational cost as compared to CCSDT. Nevertheless, as with CCSDT-3, the CCSDR(3) transition energies have a clear tendency of being too large, an error sign likely inherited from the parent CCSD model. The 0.05 eV MAE for CCSDR(3) is rather similar to the one obtained for smaller compounds when comparing to FCI (0.04 eV)[28] and is also inline with the 2009 benchmark study of Sauer et al.[24]

CCSD provides an interesting case study. The calculated MSE (+0.11 eV), indicating an overestimation of the transition energies, fits well with several previous reports.[23,28,66,69−71,76,160,256] It is, nonetheless, larger than the one determined for smaller molecules (+0.05 eV),[28] hinting that the performance of CCSD deteriorates for larger compounds. Moreover, the CCSD MAE of 0.13 eV is much smaller than the one reported by Thiel in his original work (0.49 eV)[23] but of the same order of magnitude as in the more recent study of Kánnár and Szalay performed on Thiel's set (0.18 eV for transitions with $\%T_1 > 90\%$).[69] Retrospectively, it is pretty obvious that Thiel's much larger MAE is very likely due to the CASPT2 reference values.[23] Indeed, as we have shown several times in the present study, CASPT2 transition energies tend to be significantly too low, therefore exacerbating the usual CCSD overestimation.

With a single detailed benchmark study to date,[66] the STEOM-CCSD approach has received relatively little attention, and its overall accuracy still needs to be corroborated. It is noteworthy that STEOM-CCSD provides a smaller MSE than CCSD and comparable MAE and RMSE. The spread of the error is however slightly larger as evidenced by Figure 1 and the SDE values reported in Table 12. These trends are the same as for smaller compounds.[28] For Thiel's set, Dutta and co-workers also reported a rather good performance for STEOM-CCSD with respect to the CC3/TZVP reference data, though a slightly negative MSE is obtained in their case.[66] This could well be due to the different basis sets considered in these two studies. It should be nevertheless stressed that we only consider "clean" STEOM-CCSD results in the present work (see Computational Details), therefore removing several difficult cases that are included in the CCSD statistics, e.g., the A_g excitation in butadiene, which can slightly bias the relative performance of STEOM-CCSD and CCSD.

For the three second-order methods, namely, CIS(D), ADC(2), and CC2, that are often used as reference to benchmark TD-DFT for "real-life" applications, the performance of the former method is clearly worse compared to the latter two which exhibit very similar statistical behaviors. These trends were also reported in previous works.[18,21,23,26,28,59,70,76,148] Interestingly, the CC2 MAE obtained here (0.15 eV) is significantly smaller than the one we found for smaller compounds (0.22 eV).[28] Therefore, in contrast to CCSD, CC2 performance seems to improve with molecular size. As above, Thiel's original MAE for CC2 (0.29 eV) was likely too large due to the selection of CASPT2 reference values.[23] As already noticed by Szalay's group,[69,70] although the MSE of CC2 is smaller than the one of CCSD, the

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standard deviation is significantly larger with the former model, i.e., CC2 is less consistent in terms of trends than CCSD.

Finally, one obtains a reasonably tight distribution with NEVPT2, with a net overestimation trend (MSE of 0.09 eV) and a general behavior that is in fact quite comparable to (STEOM-)CCSD in terms of average and maximal deviations. Nonetheless, we wish to recall that NEVPT2 has the obvious advantage over CCSD to be able to treat accurately ES characterized by a dominant double excitation character. As mentioned above, these were not included in the present benchmark set.

In Table 13, we report a MAE decomposition for different subsets of ES. Note that, due to implementational limitations, only singlet ES could be computed with CCSDR(3) and CCSDT-3 which explains the lack of data for triplet ES. A few interesting conclusions emerge from these results. First, the errors for singlet and triplet transitions are rather similar in all the models, except for CCSD which is significantly more effective for triplets. Dutta and co-workers observed the same trend for Thiel's set with MAEs of 0.20 and 0.11 eV for the singlet and triplet ESs, respectively.[66] Turning to the comparison between valence and Rydberg states, we find that CC2 provides a better description of the former, whereas CCSD (and higher-order methods) yields the opposite trend. In fact, CC2 has the clear tendency to overestimate valence ES energies (MSE of +0.10 eV) and to underestimate Rydberg ES energies (MSE of −0.17 eV). CCSD is found to be much more consistent with MSEs of 0.12 and 0.09 eV, respectively (see the SI). This relatively poorer performance of CC2 as compared to CCSD for Rydberg ES is again perfectly consistent with other benchmarks,[66,70] although the MAE for CC2 (0.18 eV) reported in Table 13 remains relatively small as compared to the one given in ref 70. We believe that it is likely due to the distinct types of Rydberg states considered in these two studies. Indeed, we consider here (relatively) low-lying Rydberg transitions in medium-sized molecules, while Kánnár and Szalay (mostly) investigated higher-lying Rydberg states in smaller compounds. CIS(D), ADC(2), CC2, and STEOM-CCSD better describe $n \rightarrow \pi^*$ transitions, whereas CCSD seems more suited for $\pi \rightarrow \pi^*$ transitions. The variations between the two subsets are probably not significant for the higher-order approaches. The former observation agrees well with previous results obtained for smaller compounds[28] and for Thiel's set,[23,69] whereas the latter, less expected observation is likely dependent on the selected ES subset.[23,70] Finally, the average errors obtained with NEVPT2 are rather uniform for all subsets.

Table 13. MAE (in eV) Obtained with Different Methods for Various Classes of Excited States

method	singlet	triplet	valence	Rydberg	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
CIS(D)	0.21	0.25	0.26	0.15	0.22	0.28
ADC(2)	0.15	0.13	0.13	0.17	0.08	0.17
CC2	0.16	0.14	0.14	0.18	0.08	0.19
STEOM-CCSD	0.11	0.13	0.11	0.12	0.08	0.15
CCSD	0.16	0.09	0.14	0.09	0.19	0.11
CCSDR(3)	0.05		0.07	0.02	0.08	0.06
CCSDT-3	0.05		0.06	0.03	0.08	0.04
CC3	0.01	0.01	0.01	0.01	0.01	0.02
NEVPT2	0.15	0.12	0.13	0.15	0.11	0.14

6. CONCLUDING REMARKS

We have computed highly accurate vertical transition energies for a set of 27 organic molecules containing from 4 to 6 (non-hydrogen) atoms. To this end, we employed several state-of-the-art theoretical models with increasingly large diffuse basis sets. Most of our theoretical best estimates are based on CCSDTQ (4 atoms) or CCSDT (5 and 6 atoms) excitation energies. For the vast majority of the listed excited states, the present contribution is the very first to disclose (sometimes basis-set extrapolated) CCSDT/aVTZ and (true) CC3/aVQZ transition energies as well as CC3/aVTZ oscillator strengths for each dipole-allowed transition. The present set contains a total of 238 transition energies and 90 oscillator strengths, with a reasonably good balance between singlet, triplet, valence, and Rydberg states. Among these 238 transitions, we believe that 224 are "solid" TBE; i.e., they are chemically accurate (MAE below 0.043 eV or 1 kcal·mol^{-1}) for the considered geometry. It allowed us to establish a reasonable error bar for several popular ES models with a lower computational cost: CIS(D), ADC(2), CC2, STEOM-CCSD, CCSD, CCSDR(3), CCSDT-3, CC3, and NEVPT2. It turns out that CC3 is extremely accurate and very likely should be considered as globally more robust and trustworthy than CASPT2 or NEVPT2, except for ES with a predominant double excitation character. Other methods including corrections for the triples yield a mean absolute deviation around 0.05 eV, whereas none of the second-order approaches has been found to be chemically accurate with MAEs in the 0.12−0.23 eV range.

Paraphrasing Thiel and co-workers,[23] we hope that this new set of vertical transition energies, combined or not with the ones described in our previous works,[28,72] will be useful for the community, will stimulate further developments and analyses in the field, and will provide new grounds for appraising the *pros* and *cons* of ES models already available or currently under development. Looking into a crystal ball, we can forecast that the emergence of new SCI algorithms optimized for modern supercomputer architectures will likely lead to the revision of some the present TBEs, allowing us to climb even higher on the accuracy ladder.[257]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.9b01216.

Basis set and frozen core effects, definition of the active spaces for the multiconfigurational calculations, additional details about the SCI calculations and their extrapolation, benchmark data and further statistical analysis, and geometries (PDF)

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Notes

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