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Supplemental Material for

On the Performance of DFT/MRCI-R and MR-MP2 in Spin-Orbit Coupling Calculations in Diatomics and Polyatomic Organic Molecules

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S1. On the calculation of SOMEs

In the SPOCK program all SOMEs between singlet and triplet states are initially computed with the $\hat{S}_{+1}$ operator. In this paper, the Cartesian x - and y -components of SOMEs between the $M_s = 1$ sublevel of a triplet state and a singlet state ($\langle T, M_s = 1 | \hat{\mathcal{H}}_{\text{SO } x/y} | S \rangle$) are presented. The x -components could be obtained from the initially calculated mixed-representation matrix element ($\langle T, M_s = 1 | \hat{L}_x \hat{S}_{+1} | S \rangle$) by multiplication with $-1/\sqrt{2}$ which arises from the relationship between the Cartesian and tensor forms of the spin operator, $\hat{S}_x = (\hat{S}_{-1} - \hat{S}_{+1})/\sqrt{2}$. The corresponding relationship for the $\hat{S}_y$ operator, $\hat{S}_y = i(\hat{S}_{-1} + \hat{S}_{+1})/\sqrt{2}$ leads to the same factor of $-1/\sqrt{2}$ for the y -component of SOMEs. One should note that this choice of the imaginary phase in the $\hat{S}_y$ operator is the reason for the real values of the $\hat{\mathcal{H}}_{\text{SO } y}$ matrix elements. The x and z -components are imaginary since the angular momentum operator is a purely imaginary operator. [1] The chosen z -component of the Hamiltonian couples a singlet state with the $M_s = 0$ sublevel of a triplet ($\langle T, M_s = 0 | \hat{\mathcal{H}}_{\text{SO } z} | S \rangle$). To arrive at $\langle T, M_s = 0 | \hat{L}_z \hat{S}_z | S \rangle$ starting from the “wrong” combination $\langle T, M_s = 1 | \hat{L}_z \hat{S}_{+1} | S \rangle$, one first needs to obtain the reduced matrix element (RME) by dividing the initially calculated matrix element by a 3-j symbol (only for the spin part, $\langle T, M_s = 1 | \hat{S}_{+1} | S \rangle$), and then multiplying the RME with the new, appropriate 3-j symbol (corresponding to the $\langle T, M_s = 0 | \hat{S}_0 | S \rangle$). The values of these 3-j symbols happen to be the same, $1/\sqrt{3}$, and since $\hat{S}_z = \hat{S}_0$, the conversion factor between the calculated “wrong” SOMEs and the appropriate ones is 1. The presented matrix elements between two triplet states are always of the form: $\langle T, M_s = 1 | \hat{\mathcal{H}}_{\text{SO } x/y} | T, M_s = 0 \rangle$ and $\langle T, M_s = 1 | \hat{\mathcal{H}}_{\text{SO } z} | T, M_s = 1 \rangle$ and could be obtained from the computed matrix elements by multiplying them with $1/\sqrt{2}$ in the case of x and y -components while the z -component does not need to be modified. In the tables, the imaginary unit (i) is omitted from the complex-valued matrix elements of the $\hat{\mathcal{H}}_{\text{SO } x}$ and $\hat{\mathcal{H}}_{\text{SO } z}$ operators and absolute values are presented instead.

S2. Statistical data and correlation plots

Table S1 shows the statistical data with regard the excitation energies employing the valence basis obtained at the DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory with respect to DFT/MRCI. Table S2 contains the corresponding statistical data for the SOMEs of each molecule individually and for the complete set of selected SOMEs, 278 in total. As the sign of an individual SOME depends on the (arbitrary) phases of the molecular orbitals (MOs) and of the wave functions, absolute values have been employed when computing the maximum positive and negative deviations of the SOMEs. Normalized RMSD (NRMSD), expressed as percentage, are given as the RMSD normalized by the range, i.e. the maximum value minus the minimum absolute value of the evaluated data.

Table S1. Deviations in energies of polyatomic molecules calculated with DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) with respect to DFT/MRCI. The values are given in eV and the normalized RMSD (NRMSD) is expressed as percentage.

Molecule	DFT/MRCI-R			MR-MP2(HF)			MR-MP2(BH-LYP)		
	RMSD	NRMSD	Max. (+) Max. (-)	RMSD	NRMSD	Max. (+) Max. (-)	RMSD	NRMSD	Max. (+) Max. (-)
o-benzene	0.73	15	2.26	0.73	15	2.19	0.75	15	2.20
Formaldehyde	0.12	2	0.16	0.17	3	0.36	0.23	4	0.44
Thioformaldehyde	0.59	10	0.53	1.82	6	0.37	0.34	6	0.36
Furan	0.04	1	0.06	0.09	6	0.40	0.30	7	0.42
Thiophene	0.04	1	0.07	0.06	5	0.17	0.20	6	0.10
Quinoxaline	0.10	5	0.18	0.12	16	0.32	0.39	21	0.21
Quinazoline	0.09	4	0.14	0.06	18	0.14	0.50	30	0.76
Pyranthione	0.08	2	0.06	0.19	4	0.19	0.15	5	0.11
Dithiin	0.07	2	0.11	0.11	14	0.34	0.46	19	0.76
Bithiophene	0.05	2	0.09	0.06	7	0.26	0.52	21	0.77
Nitromethane	0.39	7	0.16	1.26	8	1.15	0.47	9	1.34
Nitrobenzene	0.09	5	0.17	0.01	20	2.56	0.78	20	2.37
Dithiosuccinimide	0.58	23	0.13	1.32	15	1.99	0.69	17	1.87
Methionine	0.26	19	0.33	0.84	61	1.00	0.12	8	0.18
Isoalloxazine	0.09	5	0.15	0.04	27	0.68	0.34	22	0.69
All (161 exc states)	0.33	5	2.26	1.82	6	2.56	0.49	6	2.37
									0.81

Table S2. Deviations in SOMEs of polyatomic molecules calculated with DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) with respect to DFT/MRCI. The values are given in cm^{-1} and the normalized RMSD (NRMDS) is expressed as percentage.

Molecule	DFT/MRCI-R				MR-MP2(HF)				MR-MP2(BH-LYP)			
	RMSD	NRMDS	Max. (+)	Max. (-)	RMSD	NRMDS	Max. (+)	Max. (-)	RMSD	NRMDS	Max. (+)	Max. (-)
o-benzene	0.1	2	0.1	0.2	0.4	6	1.1	0.4	0.3	4	0.8	0.3
Formaldehyde	5.2	9	0.6	20.5	2.7	4	2.9	8.7	3.1	5	3.4	9.9
Thioformaldehyde	30.2	18	79.8	100.9	10.4	7	5.5	25.0	7.5	5	4.7	16.6
Furan	0.2	2		0.3	0.8	8	0.4	1.6	0.6	7	0.6	1.1
Thiophene	1.1	1	2.0	2.0	9.6	9	5.1	18.6	7.4	7	7.2	14.6
Quinoxaline	0.7	2	0.9	1.5	0.9	2	0.4	2.3	0.5	1	0.4	1.0
Quinazoline	0.4	2	0.2	1.1	0.9	5	1.7	2.0	0.8	5	1.8	1.8
Pyranthione	2.2	1	4.3	2.9	8.8	6	5.1	17.3	4.8	3	6.0	10.0
Dithiin	1.7	1	2.7	5.9	14.1	10	42.7	57.4	15.2	10	46.6	51.2
Bithiophene	1.4	4	0.8	4.6	8.3	27	15.8	22.9	6.5	23	12.7	15.7
Nitromethane	0.8	2	0.5	1.5	2.6	6	6.3	5.5	1.6	4	3.0	1.6
Nitrobenzene	2.4	4	6.2	2.1	2.4	4	5.7	5.0	2.5	4	5.3	5.1
Dithiosuccinimide	1.5	1		4.2	6.1	5	0.1	14.7	3.8	3	4.0	6.8
Methionine	0.7	0	0.3	2.0	5.5	7	1.4	16.5	4.2	5	1.0	12.7
Isoalloxazine	1.0	5	1.2	3.2	3.7	14	5.4	8.7	3.7	14	5.7	10.3
All (278 SOMEs)	8.3	5	79.8	100.9	8.1	5	42.7	57.4	7.7	5	46.6	51.2

Figure S1. Correlation plots of SOMEs for individual polyatomic molecules calculated with DFT-MRCI-R method vs SOMEs calculated with DFT/MRCI.

Figure S2. Correlation plots of SOMEs for individual polyatomic molecules calculated with MR-MP2(HF) method vs SOMEs calculated with DFT/MRCI.

Figure S3. Correlation plots of SOMEs for individual polyatomic molecules calculated with MR-MP2(BH-LYP) method vs SOMEs calculated with DFT/MRCI.

S3. Molecular orbitals

Figure S4. Molecular orbitals of thiophene, calculated employing the valence basis. a) HF orbitals, b) BH-LYP orbitals.

Figure S5. BH-LYP molecular orbitals of dithiin involved in the discussed states.

Figure S6. BH-LYP molecular orbitals of nitrobenzene involved in the discussed states.

S4. Individual molecules

S4.1. *o*-benzyne

Table S3. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of ***o*-benzyne**. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
1^1A_2	$\pi \rightarrow \pi_{ }^*$	3.89 (0)	3.83 (0)	4.22 (0)	4.20 (0)	
1^1B_2	$\pi \rightarrow \pi_{ }^*$	3.97 (0.002)	3.92 (0.002)	4.27 (0.002)	4.21 (0.002)	
2^1A_1	$\pi_{ }, \pi \rightarrow \pi_{ }^*, \pi^*$	4.24 (0)	6.50 (0.003) ¹	6.43 (0) ¹	6.44 (0) ¹	
1^1B_1	$\pi_{ } \rightarrow \pi_{ }^*$	5.09 (0.037)	4.94 (0.046)	5.12 (0.024)	5.01 (0.030)	5.08^a
3^1A_1	$\pi \rightarrow \pi^*$	5.28 (0.013)	5.19 (0.018) ²	4.75 (0.006) ²	4.64 (0.002) ²	
2^1B_2	$\pi_{ } \rightarrow \pi^*$	5.38 (0.005)	5.38 (0.005)	5.54 (0.004)	5.47 (0.005)	
2^1B_1	$\pi_{ }, \pi \rightarrow \pi_{ }^*, \pi^*$	5.74 (0)	7.25 (0.019) ³	7.22 (0.001) ³	7.22 (0.001) ³	
$\vdots$						
3^1B_1	$\pi \rightarrow \pi^*$	6.38 (0.183)	6.23 (0.178) ⁴	6.34 (0.106) ⁴	6.08 (0.089) ⁴	6.25^a
1^3B_1	$\pi_{ } \rightarrow \pi_{ }^*$	2.43	2.30	2.25	2.25	
1^3A_2	$\pi \rightarrow \pi_{ }^*$	3.49	3.44	3.68	3.64	
1^3B_2	$\pi \rightarrow \pi_{ }^*$	3.88	3.80	4.12	4.10	
2^3B_1	$\pi \rightarrow \pi^*$	4.18	4.03	3.93	3.82	
1^3A_1	$\pi \rightarrow \pi^*$	4.83	4.67	4.58	4.46	
2^3B_2	$\pi_{ } \rightarrow \pi^*$	5.30	5.26	5.38	5.43	
$\vdots$						
2^3A_1	$\pi_{ }, \pi \rightarrow \pi_{ }^*, \pi^*$	5.69	6.37 ⁵	6.27 ⁵	6.26 ⁵	
DFT/MRCI-R: ¹ 3^1A_1 , ² 2^1A_1 , ³ 3^1B_1 , ⁴ 2^1B_1 , ⁵ 3^3A_1 MR-MP2(HF): ¹ 3^1A_1 , ² 2^1A_1 , ³ 4^1B_1 , ⁴ 2^1B_1 , ⁵ 3^3A_1 MR-MP2(BH-LYP): ¹ 3^1A_1 , ² 2^1A_1 , ³ 4^1B_1 , ⁴ 2^1B_1 , ⁵ 3^3A_1 ^a (Absorption maximum (Ar matrix)) [2]						

Table S4.: Calculated percentage of electron configurations in the excited states wave functions of **o-benzynes** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	%	Excitation		%	Excitation		%	Excitation	
		from	to		from	to		from	to
1^1A_2	89	π_{H-1}	$\pi_{ }^*$	65	π_{H-1}	$\pi_{ }^*$	65	π_{H-1}	$\pi_{ }^*$
	3	π_{H-3}	$\pi_{ }^*$	4	π_{H-3}	$\pi_{ }^*$	3	π_{H-3}	$\pi_{ }^*$
	2	π_{H-1}, π_H	$\pi_{ }, \pi_{L+2}^*$	2	π_{H-1}, π_H	$\pi_{ }, \pi_{L+2}^*$	2	π_{H-1}, π_H	$\pi_{ }, \pi_{L+2}^*$
1^1B_2	88	π_H	$\pi_{ }^*$	65	π_H	$\pi_{ }^*$	64	π_H	$\pi_{ }^*$
	4	π_{H-1}, π_H	$\pi_{ }, \pi_{L+1}^*$	3	π_{H-1}, π_H	$\pi_{ }, \pi_{L+1}^*$	4	π_{H-1}, π_H	$\pi_{ }, \pi_{L+1}^*$
	2	π_{H-3}, π_H	$\pi_{ }, \pi_{L+1}^*$	2	π_{H-3}, π_H	$\pi_{ }, \pi_{L+1}^*$	2	π_{H-3}, π_H	$\pi_{ }, \pi_{L+1}^*$
2^1A_1	88	$\pi_{ }, \pi_H$	$\pi_{ }, \pi_{L+1}^*$	59	$\pi_{ }, \pi_H$	$\pi_{ }, \pi_{L+1}^*$	61	$\pi_{ }, \pi_H$	$\pi_{ }, \pi_{L+1}^*$
	2	$\pi_{ }, \pi_{H-1}$	$\pi_{ }, \pi_{L+2}^*$	5	$\pi_{ }, \pi_{H-1}$	$\pi_{ }, \pi_{L+2}^*$	4	$\pi_{ }, \pi_{H-1}$	$\pi_{ }, \pi_{L+2}^*$
1^1B_1	79	$\pi_{ }$	$\pi_{ }^*$	53	$\pi_{ }$	$\pi_{ }^*$	54	$\pi_{ }$	$\pi_{ }^*$
	11	π_{H-1}	π_{L+2}^*	14	π_{H-1}	π_{L+2}^*	12	π_{H-1}	π_{L+2}^*
	2	π_{H-3}	π_{L+2}^*	2	π_{H-3}	π_{L+2}^*	2	π_{H-3}	π_{L+2}^*
2^1B_2	90	$\pi_{ }$	π_{L+1}^*	66	$\pi_{ }$	π_{L+1}^*	66	$\pi_{ }$	π_{L+1}^*
	2	$\sigma_{H-5}, \pi_{ }$	$\pi_{ }, \pi_{L+1}^*$	2	$\pi_{ }, \pi_H$	π_{L+1}^*, π_{L+2}^*	2	$\pi_{ }, \pi_H$	π_{L+1}^*, π_{L+2}^*
2^1B_1	62	$\pi_{ }, \pi_{H-1}$	$\pi_{ }, \pi_{L+1}^*$	42	$\pi_{ }, \pi_{H-1}$	$\pi_{ }, \pi_{L+1}^*$	42	$\pi_{ }, \pi_{H-1}$	$\pi_{ }, \pi_{L+1}^*$
	27	$\pi_{ }, \pi_H$	$\pi_{ }, \pi_{L+2}^*$	21	$\pi_{ }, \pi_H$	$\pi_{ }, \pi_{L+2}^*$	21	$\pi_{ }, \pi_H$	$\pi_{ }, \pi_{L+2}^*$
1^3B_1	94	$\pi_{ }$	$\pi_{ }^*$	69	$\pi_{ }$	$\pi_{ }^*$	69	$\pi_{ }$	$\pi_{ }^*$
1^3A_2	88	π_{H-1}	$\pi_{ }^*$	62	π_{H-1}	$\pi_{ }^*$	62	π_{H-1}	$\pi_{ }^*$
	6	π_{H-3}	$\pi_{ }^*$	7	π_{H-3}	$\pi_{ }^*$	6	π_{H-3}	$\pi_{ }^*$
1^3B_2	91	π_H	$\pi_{ }^*$	65	π_H	$\pi_{ }^*$	64	π_H	$\pi_{ }^*$
	3	π_{H-1}, π_H	$\pi_{ }, \pi_{L+1}^*$	4	π_{H-1}, π_H	$\pi_{ }, \pi_{L+1}^*$	4	π_{H-1}, π_H	$\pi_{ }, \pi_{L+1}^*$
				2	π_{H-3}, π_H	$\pi_{ }, \pi_{L+1}^*$	2	π_{H-3}, π_H	$\pi_{ }, \pi_{L+1}^*$
2^3B_1	87	π_H	π_{L+1}^*	62	π_H	π_{L+1}^*	61	π_H	π_{L+1}^*
	5	π_{H-1}	π_{L+2}^*	6	π_{H-1}	π_{L+2}^*	6	π_{H-1}	π_{L+2}^*
1^3A_1	79	π_{H-1}	π_{L+1}^*	50	π_{H-1}	π_{L+1}^*	47	π_{H-1}	π_{L+1}^*
	12	π_H	π_{L+2}^*	16	π_H	π_{L+2}^*	18	π_H	π_{L+2}^*
				2	π_{H-3}, π_H	π_{L+1}^*, π_{L+2}^*	2	π_{H-3}, π_H	π_{L+1}^*, π_{L+2}^*
2^3B_2	92	$\pi_{ }$	π_{L+1}^*	68	$\pi_{ }$	π_{L+1}^*	67	$\pi_{ }$	π_{L+1}^*
	2	$\sigma_{H-5}, \pi_{ }$	$\pi_{ }, \pi_{L+1}^*$	2	$\pi_{ }, \pi_H$	π_{L+1}^*, π_{L+2}^*	2	$\pi_{ }, \pi_H$	π_{L+1}^*, π_{L+2}^*
2^3A_1	87	$\pi_{ }, \pi_H$	$\pi_{ }, \pi_{L+1}^*$	61	$\pi_{ }, \pi_H$	$\pi_{ }, \pi_{L+1}^*$	61	$\pi_{ }, \pi_H$	$\pi_{ }, \pi_{L+1}^*$
	3	$\pi_{ }, \pi_{H-1}$	$\pi_{ }, \pi_{L+2}^*$						

Table S5.: Calculated percentage of electron configurations in the excited states wave functions of **o-benzynes** obtained at the DFT/MRCI, and DFT/MRCI-R levels of theory. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			DFT/MRCI-R		
	%	Excitation		%	Excitation	
		from	to		from	to
1^1A_2	89	π_{H-1}	$\pi_{ }^*$	90	π_{H-1}	$\pi_{ }^*$
	3	π_{H-3}	$\pi_{ }^*$	3	π_{H-3}	$\pi_{ }^*$
	2	π_{H-1}, π_H	$\pi_{ }^*, \pi_{L+2}^*$	1	π_{H-1}, π_H	$\pi_{ }^*, \pi_{L+2}^*$
1^1B_2	88	π_H	$\pi_{ }^*$	89	π_H	$\pi_{ }^*$
	4	π_{H-1}, π_H	$\pi_{ }^*, \pi_{L+1}^*$	2	π_{H-1}, π_H	$\pi_{ }^*, \pi_{L+1}^*$
	2	π_{H-3}, π_H	$\pi_{ }^*, \pi_{L+1}^*$	2	π_{H-3}, π_H	$\pi_{ }^*, \pi_{L+1}^*$
2^1A_1	90	$\pi_{ }, \pi_H$	$\pi_{ }^*, \pi_{L+1}^*$	85	$\pi_{ }, \pi_H$	$\pi_{ }^*, \pi_{L+1}^*$
	2	$\pi_{ }, \pi_{H-1}$	$\pi_{ }^*, \pi_{L+2}^*$	3	$\pi_{ }, \pi_{H-1}$	$\pi_{ }^*, \pi_{L+2}^*$
1^1B_1	79	$\pi_{ }$	$\pi_{ }^*$	81	$\pi_{ }$	$\pi_{ }^*$
	11	π_{H-1}	π_{L+2}^*	11	π_{H-1}	π_{L+2}^*
	2	π_{H-3}	π_{L+2}^*	1	π_{H-3}	π_{L+2}^*
2^1B_2	90	$\pi_{ }$	π_{L+1}^*	92	$\pi_{ }$	π_{L+1}^*
	2	$\sigma_{H-5}, \pi_{ }$	$\pi_{ }^*, \pi_{L+1}^*$			
2^1B_1	62	$\pi_{ }, \pi_{H-1}$	$\pi_{ }^*, \pi_{L+1}^*$	71	$\pi_{ }, \pi_{H-1}$	$\pi_{ }^*, \pi_{L+1}^*$
	27	$\pi_{ }, \pi_H$	$\pi_{ }^*, \pi_{L+2}^*$	15	$\pi_{ }, \pi_H$	$\pi_{ }^*, \pi_{L+2}^*$
1^3B_1	94	$\pi_{ }$	$\pi_{ }^*$	95	$\pi_{ }$	$\pi_{ }^*$
1^3A_2	88	π_{H-1}	$\pi_{ }^*$	88	π_{H-1}	$\pi_{ }^*$
	6	π_{H-3}	$\pi_{ }^*$	5	π_{H-3}	$\pi_{ }^*$
1^3B_2	91	π_H	$\pi_{ }^*$	90	π_H	$\pi_{ }^*$
	3	π_{H-1}, π_H	$\pi_{ }^*, \pi_{L+1}^*$	2	π_{H-1}, π_H	$\pi_{ }^*, \pi_{L+1}^*$
2^3B_1	87	π_H	π_{L+1}^*	89	π_H	π_{L+1}^*
	5	π_{H-1}	π_{L+2}^*	4	π_{H-1}	π_{L+2}^*
1^3A_1	79	π_{H-1}	π_{L+1}^*	80	π_{H-1}	π_{L+1}^*
	12	π_H	π_{L+2}^*	12	π_H	π_{L+2}^*
2^3B_2	92	$\pi_{ }$	π_{L+1}^*	92	$\pi_{ }$	π_{L+1}^*
	2	$\sigma_{H-5}, \pi_{ }$	$\pi_{ }^*, \pi_{L+1}^*$			
2^3A_1	87	$\pi_{ }, \pi_H$	$\pi_{ }^*, \pi_{L+1}^*$	86	$\pi_{ }, \pi_H$	$\pi_{ }^*, \pi_{L+1}^*$
	3	$\pi_{ }, \pi_{H-1}$	$\pi_{ }^*, \pi_{L+2}^*$			

S4.2. Formaldehyde

Table S6. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of **formaldehyde** using the valence basis. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
1^1A_2	$n \rightarrow \pi^*$	3.86 (0)	3.94 (0)	3.97 (0)	4.07 (0)	3.79 ^a , 3.94^b
1^1B_2	$n \rightarrow Ryd$	8.31 (0.121)	8.14 (0.119)	8.29 (0.099)	8.35 (0.117)	
1^1B_1	$\sigma \rightarrow \pi^*$	9.00 (0.004)	9.03 (0.005)	9.17 (0.002)	9.26 (0.002)	9.0 ^c
2^1A_1	$\pi \rightarrow \pi^*$	9.42 (0.079)	9.26 (0.077)	9.43 (0.063)	9.50 (0.031)	
1^3A_2	$n \rightarrow \pi^*$	3.43	3.59	3.57	3.66	3.50 ^a , 3.50^b
1^3A_1	$\pi \rightarrow \pi^*$	5.77	5.76	6.13	6.21	
1^3B_2	$n \rightarrow Ryd$	7.77	7.69	7.75	7.80	5.82 ^a , 5.86^b
1^3B_1	$\sigma \rightarrow \pi^*$	8.23	8.36	8.40	8.45	

^a Energy-loss maximum (vapor) [3]

^b Energy-loss maximum (vapor) [4]

^c Energy-loss band origin (vapor) [5]

Table S7.: Calculated percentage of electron configurations in the excited states wave functions of **formaldehyde** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	%	Excitation		%	Excitation		%	Excitation	
		from	to		from	to		from	to
1^1A_2	93	n_H	π_L^*	78	n_H	π_L^*	82	n_H	π_L^*
	3	π_{H-1}, n_H	π_L^*, π_L^*	4	n_H	Ry_{L+5}	3	π_{H-1}, n_H	π_L^*, π_L^*
	2	n_H	Ry_{L+5}	3	π_{H-3}	π_L^*	2	π_{H-3}	π_L^*
				3	π_{H-1}, n_H	π_L^*, π_L^*			
1^1B_2	94	n_H	Ry_{L+1}	78	n_H	Ry_{L+1}	79	n_H	Ry_{L+1}
	3	π_{H-1}, n_H	π_L^*, Ry_{L+1}	3	π_{H-1}, n_H	π_L^*, Ry_{L+1}	4	π_{H-1}, n_H	π_L^*, Ry_{L+1}
				3	n_H	Ry_{L+2}	2	n_H	Ry_{L+2}
1^1B_1	93	σ_{H-2}	π_L^*	78	σ_{H-2}	π_L^*	82	σ_{H-2}	π_L^*
	3	σ_{H-2}, π_{H-1}	π_L^*, π_L^*	4	σ_{H-2}	Ry_{L+5}	5	σ_{H-2}, π_{H-1}	π_L^*, π_L^*
	2	σ_{H-2}	Ry_{L+5}	3	σ_{H-2}, π_{H-1}	π_L^*, π_L^*			
2^1A_1	67	π_{H-1}	π_L^*	59	π_{H-1}	π_L^*	53	π_{H-1}	π_L^*
	22	n_H	σ^*	13	n_H	σ^*	17	n_H	σ^*
	4	π_{H-1}, π_{H-1}	π_L^*, π_L^*	4	π_{H-1}, π_{H-1}	π_L^*, π_L^*	5	n_H, n_H	π_L^*, π_L^*
				4	n_H, n_H	π_L^*, π_L^*	5	π_{H-1}, π_{H-1}	π_L^*, π_L^*
1^3A_2	95	n_H	π_L^*	79	n_H	π_L^*	83	n_H	π_L^*
	2	n_H	Ry_{L+5}	4	n_H	Ry_{L+5}	2	π_{H-1}, n_H	π_L^*, π_L^*
				3	π_{H-3}	π_L^*	2	π_{H-3}	π_L^*
1^3A_1	97	π_{H-1}	π_L^*	84	π_{H-1}	π_L^*	89	π_{H-1}	π_L^*
	2	π_{H-1}	Ry_{L+5}	6	π_{H-1}	Ry_{L+5}	2	π_{H-1}	Ry_{L+5}
				2	π_{H-1}	Ry_{L+10}			
1^3B_2	95	n_H	Ry_{L+1}	80	n_H	Ry_{L+1}	80	n_H	Ry_{L+1}
	2	π_{H-1}, n_H	π_L^*, Ry_{L+1}	3	π_{H-1}, n_H	π_L^*, Ry_{L+1}	3	π_{H-1}, n_H	π_L^*, Ry_{L+1}
1^3B_1	95	σ_{H-2}	π_L^*	78	σ_{H-2}	π_L^*	83	σ_{H-2}	π_L^*
	2	σ_{H-2}	Ry_{L+5}	6	σ_{H-2}	Ry_{L+5}	3	σ_{H-2}, π_{H-1}	π_L^*, π_L^*
				2	σ_{H-2}, π_{H-1}	π_L^*, π_L^*			

Table S8.: Calculated percentage of electron configurations in the 2^1A_1 state wave function of **formaldehyde** obtained at the DFT/MRCI, and DFT/MRCI-R levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			DFT/MRCI-R		
	Excitation			Excitation		
	%	from	to	%	from	to
2^1A_1	67	π_{H-1}	π_L^*	56	π_{H-1}	π_L^*
	22	n_H	σ^*	19	n_H	σ^*
	4	π_{H-1}, π_{H-1}	π_L^*, π_L^*	17	n_H, n_H	π_L^*, π_L^*
				2	π_{H-1}, π_{H-1}	π_L^*, π_L^*

Table S9. Selected matrix elements (cm^{-1}) for **formaldehyde** calculated with DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) methods using the valence basis.

	SOMEs(cm^{-1})			
	DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 1^1A_1 \rangle$	62.0	59.8	64.1	64.6
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 2^1A_1 \rangle$	41.5	21.0	32.8	31.6
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } y} 1^1A_1 \rangle$	43.1	41.9	44.7	45.1
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } y} 2^1A_1 \rangle$	19.6	17.4	18.6	18.0
$\langle 1^3A_1 \hat{\mathcal{H}}_{\text{SO } z} 1^1A_2 \rangle$	53.6	52.5	55.8	56.1
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } x} 1^1A_2 \rangle$	36.3	36.3	38.2	38.3
$\langle 1^3A_1 \hat{\mathcal{H}}_{\text{SO } y} 1^1B_1 \rangle$	30.7	30.6	31.9	32.3
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } x} 1^1B_1 \rangle$	35.7	35.8	37.6	37.6
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } x} 1^1A_1 \rangle$	7.5	7.4	7.5	7.5
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } x} 2^1A_1 \rangle$	1.9	1.4	1.1	1.6
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } y} 1^1A_2 \rangle$	6.5	6.3	6.3	6.4
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } z} 1^1B_1 \rangle$	2.3	2.0	3.2	3.9
$\langle 1^3A_1 \hat{\mathcal{H}}_{\text{SO } x} 1^1B_2 \rangle$	0.3	0.3	0.5	0.4
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 1^3A_1 \rangle$	50.8	51.2	53.7	54.2
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } y} 1^3A_1 \rangle$	29.0	29.6	31.3	31.3
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } x} 1^3A_2 \rangle$	36.0	36.0	37.9	38.1

Table S10. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF), MR-MP2(BH-LYP) and CASPT2 vertical excitation energies of **formaldehyde** using the augmented basis. The CASPT2 (8,11) active space consists of following occupied/unoccupied orbitals: $1/3 a_1$, $1/2 b_1$ and $2/2 b_2$. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)						Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	CASPT2 (8,9)	CASPT2 (8,11)	
1^1A_2	$n \rightarrow \pi^*$	3.67 (0)	3.81 (0)	3.88 (0)	3.93 (0)	3.90	3.99 (0)	3.79^a , 3.94^b
1^1B_2	$n \rightarrow 3s$	7.02 (0.032)	6.93 (0.034)	6.99 (0.010)	6.99 (0.023)	6.77	6.87 (0.035)	7.09^c
2^1B_2	$n \rightarrow 3p_z$	7.86 (0.039)	7.84 (0.032)	7.92 (0.026)	8.17 (0.034)	7.68	7.76 (0.027)	8.13^c
2^1A_1	$n \rightarrow 3p_y$	7.96 (0.054)	7.88 (0.052)	7.99 (0.035)	8.04 (0.042)	7.78	7.84 (0.058)	7.98^c
2^1A_2	$n \rightarrow 3p_x$	8.40 (0)	8.26 (0)	8.14 (0)	8.24 (0)	7.95	8.00 (0)	8.37^d
1^1B_1	$\sigma \rightarrow \pi^*$	8.81 (0.004)	8.90 (0.005)	9.12 (0.006)	9.20 (0.002)	9.21	9.43 (0.014)	9.0^e
$\vdots$								
4^1A_1	$\pi \rightarrow \pi^*$	9.51 (0.193)	9.50 (0.197) [†]	9.64 (0.129)	9.64 (0.126)	9.33	10.41 (0.129) ⁿ	
$\vdots$								
5^1A_1	$n^2 \rightarrow \pi^{*2}$	11.06 (0.008)	9.20 (0.022) [‡]	10.67 (0.007)	10.75 (0.016)	10.29 ^m	10.87(0.030) ^p	3.50^a , 3.50^b 5.82^a , 5.86^b
1^3A_2	$n \rightarrow \pi^*$	3.23	3.46	3.42	3.46	3.45	3.56	
1^3A_1	$\pi \rightarrow \pi^*$	5.58	5.71	6.13	6.18	6.04	6.04	
1^3B_2	$n \rightarrow 3s$	6.78	6.75	6.79	6.79	6.65	6.75	
2^3B_2	$n \rightarrow 3p_z$	7.67	7.71	7.82	7.86	7.57	7.65	
2^3A_1	$n \rightarrow 3p_y$	7.76	7.72	7.90	8.11	7.67	7.73	
1^3B_1	$\sigma \rightarrow \pi^*$	8.01	8.23	8.33	8.42	8.36	8.56	
2^3A_2	$n \rightarrow 3p_x$	8.32	8.20	8.20	8.23	7.97	8.03	

[†] 5^1A_1

[‡] 4^1A_1

^m Mixed with $\pi - 3p_x$, positive linear combination at 11.07

ⁿ Mixture of $\pi - \pi^*$ (51%), $\pi - 3p_x$ (32%), and $n^2 - \pi^{*2}$ (6%)

^p Mixture of $n^2 - \pi^{*2}$ (43%), $\pi - 3p_x$ (39%), and $\pi - \pi^*$ (4%). There is

another, almost degenerate state at 10.81 eV with oscillator strengths of 0.104,

comprised of $n^2 - \pi^{*2}$ (31%), $\pi - \pi^*$ (25%) and $\pi - 3p_x$ (21%) excitations

^a Energy-loss maximum (vapor) [3]

^b Energy-loss maximum (vapor) [4]

^c Absorption band origin (vapor) [6]

^d Energy-loss band origin (vapor) [4]

^e Energy-loss band origin (vapor) [5]

Table S11.: Calculated percentage of electron configurations in the excited states wave functions of **formaldehyde** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	Excitation			Excitation			Excitation		
	%	from	to	%	from	to	%	from	to
1^1A_2	81	n_H	π_L^*	67	n_H	π_L^*	74	n_H	π_L^*
	10	n_H	$3p_x(c)$	11	n_H	$3p_x(c)$	5	n_H	$3p_x(c)$
1^1B_2	85	n_H	$3s(c)$	58	n_H	$3s(c)$	75	n_H	$3s(c)$
	7	n_H	$3p_z(c)$	12	n_H	$3s(o)$	5	n_H	$3p_z(c)$
				12	n_H	$3p_z(c)$			
1^1B_1	82	σ_{H-2}	π_L^*	71	σ_{H-2}	π_L^*	74	σ_{H-2}	π_L^*
	11	σ_{H-2}	$3p_x(c)$	9	σ_{H-2}	$3p_x(c)$	7	σ_{H-2}	$3p_x(c)$
4^1A_1	53	π_{H-1}	π_L^*	43	π_{H-1}	π_L^*	61	π_{H-1}	π_L^*
	25	n_H	$3p_y(o)$	19	π_{H-1}	$3p_x(c)$	6	n_H	$3p_y(o)$
	5	π_{H-1}	$3p_x(c)$	7	n_H	$3p_y(o)$	6	π_H, π_H	π_L^*, π_L^*
							5	π_{H-1}, π_{H-1}	π_L^*, π_L^*
5^1A_1	72	n_H^2	π_L^{2*}	54	n_H^2	π_L^{2*}	64	n_H^2	π_L^{2*}
	13	n_H^2	$\pi_L^*, 3p_x$	17	n_H^2	$\pi_L^*, 3p_x$	6	π_{H-1}	π_L^*
							5	n_H^2	$\pi_L^*, 3p_x$
1^3A_2	83	n_H	π_L^*	70	n_H	π_L^*	75	n_H	π_L^*
	10	n_H	$3p_x(c)$	11	n_H	$3p_x(c)$	6	n_H	$3p_x(c)$
1^3A_1	84	π_{H-1}	π_L^*	75	π_{H-1}	π_L^*	78	π_{H-1}	π_L^*
	11	π_{H-1}	$3p_x(c)$	10	π_{H-1}	$3p_x(c)$	9	π_{H-1}	$3p_x(c)$
1^3B_2	84	n_H	$3s(c)$	58	n_H	$3s(c)$	75	n_H	$3s(c)$
	7	n_H	σ_{L+10}^*	10	n_H	$3p_z(c)$			
				8	n_H	$3s(o)$			
1^3B_1	82	σ_{H-2}	π_L^*	72	σ_{H-2}	π_L^*	75	σ_{H-2}	π_L^*
	11	σ_{H-2}	$3p_x(c)$	9	σ_{H-2}	$3p_x(c)$	7	σ_{H-2}	$3p_x(c)$

The orbitals presented in the table are labeled according to the order obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different:

The π_L^* bh-lyp orbital corresponds to the π_{L+9}^* hf orbital.

Table S12.: Calculated percentage of electron configurations in the excited states wave functions of **formaldehyde** obtained at the DFT/MRCI-R and CASPT2 (8,11) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

State	DFT/MRCI-R			CASPT2 (8,11)		
	%	Excitation		%	Excitation	
		from	to		from	to
1^1A_2	83	n_H	π_L^*	95	n_H	π_L^*
	10	n_H	$3p_x(c)$			
1^1B_2	87	n_H	$3s(c)$	94	n_H	$3s(c)$
	4	n_H	$3p_z(c)$			
1^1B_1	82	σ_{H-2}	π_L^*	96	σ_{H-2}	π_L^*
	10	σ_{H-2}	$3p_x(c)$			
4^1A_1	53	π_{H-1}	π_L^*	51	π_{H-1}	π_L^*
	13	n_H^2	π_L^{2*}			
	12	n_H	$3p_y(o)$		6	n_H^2
5^1A_1	52	n_H^2	π_L^{2*}	43	n_H^2	π_L^{2*}
	17	n_H	$3p_y(o)$			
	12	n_H^2	$\pi_L^*, 3p_x$		π_{H-1}	$3p_x(c)$
	5	π_{H-1}	π_L^*			
1^3A_2	84	n_H	π_L^*	94	n_H	π_L^*
	10	n_H	$3p_x(c)$			
1^3A_1	86	π_{H-1}	π_L^*	97	π_{H-1}	π_L^*
	10	π_{H-1}	$3p_x(c)$			
1^3B_2	85	n_H	$3s(c)$	94	n_H	$3s(c)$
	6	n_H	σ_{L+10}^*			
1^3B_1	83	σ_{H-2}	π_L^*	96	σ_{H-2}	π_L^*
	11	σ_{H-2}	$3p_x(c)$			

S4.3. Thioformaldehyde

Table S13. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of **thioformaldehyde** using the valence basis. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
1^1A_2	$n \rightarrow \pi^*$	2.18 (0)	2.22 (0)	2.11 (0)	2.10 (0)	6.2^a
2^1A_1	$\pi \rightarrow \pi^*$	6.49 (0.213)	6.50 (0.177) [†]	6.40 (0.162)	6.32 (0.151)	
1^1B_1	$n \rightarrow \sigma^*$	6.88 (0.001)	6.87 (0.001)	7.17 (0)	7.06 (0.001)	
1^1B_2	$\sigma \rightarrow \pi^*$	6.91 (0.019)	6.90 (0.021)	6.75 (0.010)	6.71 (0.008)	
2^1A_2	$\pi, n \rightarrow \pi^{*2}$	7.18 (0)	7.71 (0)	7.55 (0)	7.54 (0)	
3^1A_1	$n^2 \rightarrow \pi^{*2}$	7.89 (0.011)	6.07 (0.074) [‡]	7.29 (0.015)	7.25 (0.015)	
1^3A_2	$n \rightarrow \pi^*$	1.86	1.93	1.81	1.81	
1^3A_1	$\pi \rightarrow \pi^*$	3.31	3.24	3.34	3.32	
1^3B_2	$\sigma \rightarrow \pi^*$	6.06	6.13	5.84	5.80	
1^3B_1	$n \rightarrow \sigma^*$	6.36	6.41	6.53	6.43	
$\vdots$						
2^3A_2	$\pi, n \rightarrow \pi^{*2}$	7.79	7.31	7.08	7.06	

^a Peak maximum [7]

[†] 3^1A_1

[‡] 2^1A_1

Table S14.: Calculated percentage of electron configurations in the excited states wave functions of **thioformaldehyde** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	Excitation			Excitation			Excitation		
	%	from	to	%	from	to	%	from	to
1^1A_2	92	n_H	π_L^*	79	n_H	π_L^*	80	n_H	π_L^*
	7	π_{H-1}, n_H	π_L^*, π_L^*	6	π_{H-1}, n_H	π_L^*, π_L^*	7	π_{H-1}, n_H	π_L^*, π_L^*
2^1A_1	89	π_{H-1}	π_L^*	72	π_{H-1}	π_L^*	72	π_{H-1}	π_L^*
	2	n_H, n_H	π_L^*, π_L^*	5	n_H, n_H	π_L^*, π_L^*	4	n_H, n_H	π_L^*, π_L^*
1^1B_1	88	n_H	σ_{L+1}^*	73	n_H	σ_{L+1}^*	76	n_H	σ_{L+1}^*
	4	n_H	σ_{L+4}^*	6	n_H	σ_{L+4}^*	3	π_{H-1}, n_H	π_L^*, σ_{L+1}^*
	3	π_{H-1}, n_H	π_L^*, σ_{L+1}^*	3	π_{H-1}, n_H	π_L^*, σ_{L+1}^*	3	n_H	σ_{L+4}^*
1^1B_2	94	σ_{H-2}	π_L^*	78	σ_{H-2}	π_L^*	79	σ_{H-2}	π_L^*
	2	σ_{H-2}, π_{H-1}	π_L^*, π_L^*	3	σ_{H-2}, π_{H-1}	π_L^*, π_L^*	3	σ_{H-2}, π_{H-1}	π_L^*, π_L^*
2^1A_2	72	π_{H-1}, n_H	π_L^*, π_L^*	41	π_{H-1}, n_H	π_L^*, π_L^*	43	π_{H-1}, n_H	π_L^*, π_L^*
	18	σ_{H-3}	π_L^*	33	σ_{H-3}	π_L^*	32	σ_{H-3}	π_L^*
				5	σ_{H-3}, π_{H-1}	π_L^*, π_L^*	5	σ_{H-3}, π_{H-1}	π_L^*, π_L^*
	5	n_H	π_L^*	4	n_H	π_L^*	4	n_H	π_L^*
3^1A_1	86	n_H, n_H	π_L^*, π_L^*	70	n_H, n_H	π_L^*, π_L^*	70	n_H, n_H	π_L^*, π_L^*
	8	n_H, σ_{H-3}	π_L^*, π_L^*	7	n_H, σ_{H-3}	π_L^*, π_L^*	9	n_H, σ_{H-3}	π_L^*, π_L^*
	2	π_{H-1}	π_L^*	4	π_{H-1}	π_L^*	4	π_{H-1}	π_L^*
1^3A_2	96	n_H	π_L^*	82	n_H	π_L^*	83	n_H	π_L^*
1^3A_1	99	π_{H-1}	π_L^*	86	π_{H-1}	π_L^*	88	π_{H-1}	π_L^*
1^3B_2	97	σ_{H-2}	π_L^*	82	σ_{H-2}	π_L^*	82	σ_{H-2}	π_L^*
1^3B_1	78	n_H	σ_{L+1}	56	n_H	σ_{L+1}	64	n_H	σ_{L+1}
	9	n_H	σ_{L+4}	16	n_H	σ_{L+4}	10	n_H	σ_{L+4}
	7	n_H	σ_{L+3}	6	n_H	σ_{L+3}	5	n_H	σ_{L+3}
2^3A_2	51	σ_{H-3}	π_L^*	63	π_{H-1}, n_H	π_L^*, π_L^*	64	π_{H-1}, n_H	π_L^*, π_L^*
	44	π_{H-1}, n_H	π_L^*, π_L^*	14	σ_{H-3}	π_L^*	14	σ_{H-3}	π_L^*

Table S15.: Calculated percentage of electron configurations in the discussed wave functions of **thioformaldehyde** obtained at the DFT/MRCI, and DFT/MRCI-R levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			DFT/MRCI-R		
	%	Excitation		%	Excitation	
		from	to		from	to
2^1A_1	89	π_{H-1}	π_L^*	65	π_{H-1}	π_L^*
	2	n_H, n_H	π_L^*, π_L^*	28	n_H, n_H	π_L^*, π_L^*
2^1A_2	72	π_{H-1}, n_H	π_L^*, π_L^*	63	π_{H-1}, n_H	π_L^*, π_L^*
	18	σ_{H-3}	π_L^*	29	σ_{H-3}	π_L^*
	5	n_H	π_L^*	3	n_H	π_L^*
3^1A_1	86	n_H, n_H	π_L^*, π_L^*	66	n_H, n_H	π_L^*, π_L^*
	8	n_H, σ_{H-3}	π_L^*, π_L^*	28	π_{H-1}	π_L^*
	2	π_{H-1}	π_L^*	2	n_H, σ_{H-3}	π_L^*, π_L^*
2^3A_2	51	σ_{H-3}	π_L^*	79	π_{H-1}, n_H	π_L^*, π_L^*
	44	π_{H-1}, n_H	π_L^*, π_L^*	14	σ_{H-3}	π_L^*

Table S16. Selected matrix elements (cm^{-1}) for **thioformaldehyde** calculated with DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) methods using the valence basis.

	SOMEs(cm^{-1})			
	DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 1^1A_1 \rangle$	180.3	178.2	163.6	168.8
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 2^1A_1 \rangle$	99.4	179.2	74.4	83.0
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 3^1A_1 \rangle$	156.8	55.8	148.5	147.8
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } y} 1^1A_1 \rangle$	66.3	63.8	57.7	58.9
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } y} 2^1A_1 \rangle$	16.5	15.9	18.3	17.4
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } y} 3^1A_1 \rangle$	6.9	6.7	8.3	5.6
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } x} 1^1A_1 \rangle$	105.6	105.2	98.2	101.6
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } x} 2^1A_1 \rangle$	76.0	60.9	67.2	70.1
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } x} 3^1A_1 \rangle$	6.3	44.3	11.8	11.0
$\langle 1^3A_1 \hat{\mathcal{H}}_{\text{SO } z} 1^1A_2 \rangle$	168.2	163.2	155.5	160.9
$\langle 1^3A_1 \hat{\mathcal{H}}_{\text{SO } z} 2^1A_2 \rangle$	89.6	95.8	70.1	73.0
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } x} 1^1A_2 \rangle$	32.4	31.3	27.6	28.3
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } y} 1^1A_2 \rangle$	105.8	106.3	99.7	103.2
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } x} 1^1B_1 \rangle$	23.4	22.6	16.2	17.1
$\langle 1^3A_1 \hat{\mathcal{H}}_{\text{SO } x} 1^1B_2 \rangle$	88.0	85.8	81.0	81.6
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } y} 1^1B_2 \rangle$	104.7	104.9	96.5	99.6
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 1^3A_1 \rangle$	157.2	158.4	148.4	154.4
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } x} 1^3A_2 \rangle$	28.9	27.5	23.1	22.9
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } x} 1^3A_1 \rangle$	82.0	82.5	78.6	81.8
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } y} 1^3A_2 \rangle$	106.9	106.6	100.4	103.6

Table S17. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF), MR-MP2(BH-LYP) and CASPT2 vertical excitation energies of **thioformaldehyde** using the augmented basis. The CASPT2 (8,11) active space consists of following occupied/unoccupied orbitals: $1/3 a_1$, $1/2 b_2$ and $2/2 b_1$. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	CASPT2 (8,11)
1^1A_2	$n \rightarrow \pi^*$	2.16 (0)	2.20 (0)	2.10 (0)	2.16 (0)	2.11 (0)
1^1B_1	$n \rightarrow 4s$	5.67 (0.009)	5.67 (0.009)	6.07 (0.015)	5.99 (0.016)	5.84 (0.027)
2^1B_1	$n \rightarrow 4p_z$	6.35 (0.039)	6.35 (0.039)	6.83 (0.030)	6.73 (0.033)	6.57 (0.024)
2^1A_1	$\pi \rightarrow \pi^*$	6.46 (0.243)	6.48 (0.216) ¹	6.30 (0.178)	6.50 (0.146) ¹	6.29 (0.126) ^m
3^1A_1	$n \rightarrow 4p_x$	6.53 (0.014)	6.53 (0) ²	7.04 (0.003)	6.45 (0.046) ²	6.78 (0.019)
2^1A_2	$n \rightarrow 4p_y$	6.67 (0)	6.65 (0)	7.19 (0)	7.08 (0)	6.94 (0)
1^1B_2	$\sigma \rightarrow \pi^*$	6.89 (0.016)	6.89 (0.018)	6.72 (0.008)	6.78 (0.002)	7.15 (0.058)
3^1A_2	$\pi, n \rightarrow \pi^{*2}$	7.19 (0)	7.70 (0) ³	7.61 (0)	7.58 (0)	7.66 (0)
$\vdots$						
5^1A_1	$n^2 \rightarrow \pi^{*2}$	7.84 (0.006)	6.06 (0.076) ⁴	7.27 (0.010) ¹	7.26 (0.019) ³	7.11 (0.086) ⁿ
1^3A_2	$n \rightarrow \pi^*$	1.84	1.92	1.81	1.89	1.84
1^3A_1	$\pi \rightarrow \pi^*$	3.29	3.23	3.33	3.37	3.34
1^3B_1	$n \rightarrow 4s$	5.54	5.54	5.93	5.85	5.75
1^3B_2	$\sigma \rightarrow \pi^*$	6.04	6.12	5.81	5.85	6.24
$\vdots$						
4^3A_2	$\pi, n \rightarrow \pi^{*2}$	7.77	7.28 ⁵	7.11 ²	7.24	7.19
DFT-/MRCI-R: $1^1 3^1A_1, 2^1 4^1A_1, 3^1 4^1A_2, 4^1 2^1A_1, 5^1 3^1A_2$						
MR-MP2(HF): $1^1 4^1A_1, 2^1 2^3A_2$						
MR-MP2(BH-LYP): $1^1 3^1A_1, 2^1 2^1A_1, 3^1 4^1A_1$						
^m Mixture of $\pi - \pi^*$ (50%) and $n^2 - \pi^{*2}$ (37%)						
ⁿ Mixture of $n^2 - \pi^{*2}$ (51%) and $\pi - \pi^*$ (36%)						
^a Vertical transition (absorption) [8]						
^b Absorption band origin [9]						
^c Absorption peak maximum (vapor) [7]						

Table S18.: Calculated percentage of electron configurations in the excited states wave functions of **thioformaldehyde** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
		Excitation			Excitation			Excitation	
	%	from	to	%	from	to	%	from	to
1^1A_2	91	n_H	π_L^*	51	n_H	π_L^*	78	n_H	π_L^*
	6	π_{H-1}, n_H	π_L^*, π_L^*	28	n_H	$\pi_{L+9}^* \dagger$	8	π_{H-1}, n_H	π_L^*, π_L^*
2^1A_1	87	π_{H-1}	π_L^*	50	π_{H-1}	π_L^*	36	π_{H-1}	π_L^*
				21	π_{H-1}	π_{L+9}^*	36	n_H	$4px$
1^1B_1	86	n_H	$4s(c)$	52	n_H	$4s(c)$	73	n_H	$4s(c)$
	5	n_H	σ_{L+10}^*	24	n_H	$4s(s)$	7	n_H	$4p_z$
1^1B_2	92	σ_{H-2}	π_L^*	49	σ_{H-2}	π_L^*	73	σ_{H-2}	π_L^*
				29	σ_{H-2}	π_{L+9}^*	6	n_H	$3d_{xy}$
3^1A_2	66	π_{H-1}, n_H	π_L^*, π_L^*	27	σ_{H-3}	π_L^*	38	π_{H-1}, n_H	π_L^*, π_L^*
	18	σ_{H-3}	π_L^*	14	π_{H-1}, n_H	π_L^*, π_L^*	34	σ_{H-3}	π_L^*
	6	n_H	π_L^*	13	π_{H-1}, n_H	π_L^*, π_{L+9}^*	5	σ_{H-3}, π_{H-1}	π_L^*, π_L^*
				16	σ_{H-3}	π_{L+9}^*			
5^1A_1	85	n_H^2	π_L^{2*}	28	n_H^2	π_L^{2*}	68	n_H, n_H	π_L^*, π_L^*
	8	n_H, σ_{H-3}	π_L^*, π_L^*	27	n_H^2	π_L^*, π_{L+9}^*	9	n_H, σ_{H-3}	π_L^*, π_L^*
		π_{H-1}	π_L^*				6	π_{H-1}	π_L^*
1^3A_2	95	n_H	π_L^*	52	n_H	π_L^*	82	n_H	π_L^*
				29	n_H	π_{L+9}^*			
1^3A_1	98	π_{H-1}	π_L^*	52	π_{H-1}	π_L^*	88	π_{H-1}	π_L^*
				34	π_{H-1}	π_{L+9}^*			
1^3B_1	81	n_H	$4s(c)$	48	n_H	$4s(c)$	71	n_H	$4s(c)$
	11	n_H	σ_{L+10}^*	23	n_H	$4s(S)$	5	n_H	p_z
				6	n_H	σ_{L+10}^*			
1^3B_2	96	σ_{H-2}	π_L^*	50	σ_{H-2}	π_L^*	82	σ_{H-2}	π_L^*
				32	σ_{H-2}	π_{L+9}^*			
4^3A_2	50	σ_{H-3}	π_L^*	19	π_{H-1}, n_H	π_L^*, π_L^*	42	n_H	$3d_{yz}$
	41	π_{H-1}, n_H	π_L^*, π_L^*	17	π_{H-1}, n_H	π_L^*, π_{L+9}^*	28	π_{H-1}, n_H	π_L^*, π_L^*
				21	σ_{H-3}	π_L^*	5	σ_{H-3}	π_L^*
				13	σ_{H-3}	π_{L+9}^*			
				5	n_H	π_{L+9}^*			

$\dagger$ HF orbital which valence part is the same as π_L^* (BH-LYP), but with the opposite phase.
 The π^* and d_{yz} orbitals are mixed at the HF level.
 The orbitals presented in the table are labeled according to the order obtained within the DFT theory.
 In the following cases the ordering of the Hartree-Fock orbitals is different:
 The π_L^* bh-lyp orbital corresponds to the π_{L+4}^* hf orbital.

Table S19.: Calculated percentage of electron configurations in the discussed wave functions of **thioformaldehyde** obtained at the DFT/MRCI-R, and CASPT2 (8,11) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

State	DFT/MRCI-R			CASPT2 (8,11)		
	%	Excitation		%	Excitation	
		from	to		from	to
1^1A_2	93	n_H	π_L^*	92	n_H	π_L^*
	5	π_{H-1}, n_H	π_L^*, π_L^*			
2^1A_1	54	π_{H-1}	π_L^*	50	π_{H-1}	π_L^*
	22	n_H^2	π_L^{2*}	37	n_H^2	π_L^{2*}
	16	n_H	$4p_x$			
1^1B_1	87	n_H	$4s(c)$	92	n_H	$4s(c)$
	5	n_H	σ_{L+10}^*			
1^1B_2	94	σ_{H-2}	π_L^*	94	σ_{H-2}	π_L^*
3^1A_2	59	π_{H-1}, n_H	π_L^*, π_L^*	60	π_{H-1}, n_H	π_L^*, π_L^*
	28	σ_{H-3}	π_L^*	25	σ_{H-3}	π_L^*
		n_H	π_L^*			
5^1A_1	65	n_H^2	π_L^{2*}	51	n_H^2	π_L^{2*}
	28	π_{H-1}	π_L^*	36	π_{H-1}	π_L^*
	2	n_H, σ_{H-3}	π_L^*, π_L^*			
1^3A_2	95	n_H	π_L^*	95	n_H	π_L^*
1^3A_1	98	π_{H-1}	π_L^*	97	π_{H-1}	π_L^*
1^3B_1	83	n_H	$4s(c)$	93	n_H	$4s(c)$
	9	n_H	σ_{L+10}^*			
1^3B_2	96	σ_{H-2}	π_L^*	94	σ_{H-2}	π_L^*
4^3A_2	65	π_{H-1}, n_H	π_L^*, π_L^*	75	π_{H-1}, n_H	π_L^*, π_L^*
	12	σ_{H-3}	π_L^*	12	σ_{H-3}	π_L^*
	11	n_H	$3d_yz$			

S4.4. FuranTable S20. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of **furan** using the valence basis. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
2^1A_1	$\pi \rightarrow \pi^*$	6.40 (0)	6.43 (0.001)	6.20 (0.001)	6.12 (0.002)	6.04^{a,b} , 6.06 ^c
1^1B_1	$\pi \rightarrow \pi^*$	6.43 (0.235)	6.34 (0.253)	6.42 (0.165)	6.30 (0.163)	
1^1A_2	$\pi \rightarrow Ryd$	7.46 (0)	7.48 (0)	7.75 (0)	7.81 (0)	
2^1A_2	$\pi \rightarrow Ryd$	8.03 (0)	8.06 (0)	8.24 (0)	8.44 (0)	
1^1B_2	$\pi \rightarrow Ryd$	8.13 (0.014)	8.14 (0.014)	8.50 (0.020)	8.50 (0.022)	7.82 ^c , 7.80^a
3^1A_1	$\pi \rightarrow \pi^*$	8.28 (0.698)	8.23 (0.772)	7.97 (0.415)	7.84 (0.390)	
1^3B_1	$\pi \rightarrow \pi^*$	4.00	4.01	4.08	4.08	
1^3A_1	$\pi \rightarrow \pi^*$	5.19	5.20	5.23	5.20	
2^3A_1	$\pi \rightarrow \pi^*$	6.67	6.63	6.45	6.37	5.20^d 5.22 ^c
2^3B_1	$\pi \rightarrow \pi^*$	7.25	7.20	7.09	7.05	
1^3A_2	$\pi \rightarrow Ryd$	7.33	7.37	7.66	7.66	
2^3A_2	$\pi \rightarrow Ryd$	7.69	7.75	7.91	7.84	
1^3B_2	$\pi \rightarrow Ryd$	7.97	8.02	8.37 ¹	8.39 ¹	

MRMP2 (HF)¹2³B₂MRMP2 (BH-LYP)¹2³B₂^a VUV maximum (gas) [10]^b Electron energy-loss maximum (gas) [11]^c Electron energy-loss maximum (gas) [12]^d Electron impact maximum (gas)[13]

Table S21.: Calculated percentage of electron configurations in the excited states wave functions of **fulran** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	%	Excitation		%	Excitation		%	Excitation	
		from	to		from	to		from	to
2^1A_1	45	π_{H-1}	π_L^*	31	π_{H-1}	π_L^*	31	π_{H-1}	π_L^*
	37	π_H	π_{L+2}^*	26	π_H	π_{L+2}^*	27	π_H	π_{L+2}^*
	5	π_{H-1}, π_H	π_L^*, π_{L+2}^*	6	π_H, π_H	π_L^*, π_L^*	6	π_H, π_H	π_L^*, π_L^*
	4	π_H, π_H	π_L^*, π_L^*	4	π_{H-1}, π_H	π_L^*, π_{L+2}^*	5	π_{H-1}, π_H	π_L^*, π_{L+2}^*
	2	π_H, π_H	π_{L+2}^*, π_{L+2}^*	2	π_H, π_H	π_{L+2}^*, π_{L+2}^*	2	π_H, π_H	π_{L+2}^*, π_{L+2}^*
				2	π_{H-1}, π_{H-1}	π_L^*, π_L^*	2	π_{H-1}, π_{H-1}	π_L^*, π_L^*
1^1B_1	95	π_H	π_L^*	74	π_H	π_L^*	72	π_H	π_L^*
1^1A_2	89	π_H	Ry_{L+1}	68	π_H	Ry_{L+1}	71	π_H	Ry_{L+1}
	4	π_H	Ry_{L+6}	4	π_H	Ry_{L+6}			
				2	π_{H-1}	Ry_{L+4}			
1^1B_2	85	π_H	Ry_{L+4}	56	π_H	Ry_{L+4}	61	π_H	Ry_{L+4}
	9	π_{H-1}	Ry_{L+1}	10	π_H	Ry_{L+5}	11	π_{H-1}	Ry_{L+1}
				9	π_{H-1}	Ry_{L+1}	4	π_H	Ry_{L+5}
1^3B_1	92	π_H	π_L^*	69	π_H	π_L^*	70	π_H	π_L^*
	4	π_{H-1}	π_{L+2}^*	4	π_{H-1}	π_{L+2}^*	5	π_{H-1}	π_{L+2}^*
1^3A_1	51	π_{H-1}	π_L^*	36	π_{H-1}	π_L^*	37	π_H	π_{L+2}^*
	44	π_H	π_{L+2}^*	35	π_H	π_{L+2}^*	35	π_{H-1}	π_L^*
	2	π_{H-1}, π_H	π_L^*, π_{L+2}^*	2	π_{H-1}, π_H	π_L^*, π_{L+2}^*	3	π_{H-1}, π_H	π_L^*, π_{L+2}^*
1^3A_2	89	π_H	Ry_{L+1}	68	π_H	Ry_{L+1}	69	π_H	Ry_{L+1}
	4	π_H	Ry_{L+6}	3	π_H	Ry_{L+6}	3	π_H	Ry_{L+6}
	2	π_{H-1}	Ry_{L+4}	2	π_{H-1}	Ry_{L+4}	2	π_{H-1}	Ry_{L+4}
1^3B_2	84	π_H	Ry_{L+4}	55	π_H	Ry_{L+4}	62	π_H	Ry_{L+4}
	11	π_{H-1}	Ry_{L+1}	11	π_{H-1}	Ry_{L+1}	12	π_{H-1}	Ry_{L+1}
				8	π_H	Ry_{L+5}			

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:

The π_{L+2}^* bh-lyp orbital corresponds to the π_{L+5}^* hf orbital;

The Ry_{L+4} bh-lyp orbital corresponds to the Ry_{L+2} hf orbital;

The Ry_{L+5} bh-lyp orbital corresponds to the Ry_{L+4} hf orbital.

Table S22. Selected matrix elements (cm^{-1}) for **furan** calculated with DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) methods using the valence basis.

	SOMEs(cm^{-1})			
	DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 1^1A_1 \rangle$	9.6	9.3	9.1	9.1
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 2^1A_1 \rangle$	1.1	1.0	1.0	1.2
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } x} 1^1A_2 \rangle$	5.2	5.0	4.4	4.7
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } x} 1^1B_1 \rangle$	4.6	4.4	3.4	3.5
$\langle 1^3A_1 \hat{\mathcal{H}}_{\text{SO } x} 1^1B_2 \rangle$	3.8	3.7	4.1	4.3
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } y} 1^1B_2 \rangle$	0.3	0.2	0.1	0.1
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } z} 1^1B_2 \rangle$	9.4	9.3	7.8	8.2
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 1^3A_1 \rangle$	1.1	0.9	1.4	1.1
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } x} 1^3A_2 \rangle$	5.1	5.0	4.4	4.7
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } x} 1^3A_1 \rangle$	3.9	3.7	4.2	4.2

Table S23. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF), MR-MP2(BH-LYP) and CASPT2 (6,9) vertical excitation energies of **furan** using the augmented basis. The CASPT2 active space consists of following occupied/unoccupied orbitals: $0/2\ a_1$, $0/1\ b_1$, $2/2\ b_2$ and $1/1\ a_2$. The oscillator strengths are given in the parentheses.

[illegible]

Table S24.: Calculated percentage of electron configurations in the excited states wave functions of **furan** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

DFT/MRCI				MRMP2			MRMP2		
(BH-LYP)				(HF)			(BH-LYP)		
Excitation				Excitation			Excitation		
State	%	from	to	%	from	to	%	from	to
2^1A_1	32	π_H	π_{L+10}^*	30	π_{H-1}	π_{L+9}^*	26	π_H	π_{L+10}^*
	28	π_{H-1}	π_{L+3}^*/p_y	26	π_H	π_{L+10}^*	19	π_{H-1}	π_{L+3}^*/p_y
	23	π_{H-1}	π_{L+9}^*/p_y	6	π_H, π_H	π_{L+9}^*, π_{L+9}^*	14	π_{H-1}	π_{L+9}^*/p_y
1^1B_1	71	π_H	π_{L+3}^*/p_y	59	π_H	$3p_y$	50	π_H	π_{L+3}^*/p_y
	24	π_H	π_{L+9}^*/p_y	14	π_H	π_{L+9}^*	26	π_H	$3p_y$
1^1A_2	90	π_H	$3s$	57	π_H	$3s$	68	π_H	$3s$
				13	π_H	$3p_z$			
1^1B_2	91	π_H	$3p_x$	66	π_H	$3p_x$	71	π_H	$3p_x$
		π_{H-1}	Ry_{L+1}	7	π_H	$3d_{xz}$			
1^3B_1	46	π_H	π_{L+3}^*/p_y	67	π_H	π_{L+9}^*	36	π_H	π_{L+9}^*/p_y
	46	π_H	π_{L+9}^*/p_y	5	π_{H-1}	π_{L+10}^*	36	π_H	π_{L+9}^*/p_y
1^3A_1	36	π_H	π_{L+10}^*	39	π_H	π_{L+10}^*	38	π_H	π_{L+10}^*
	30	π_{H-1}	π_{L+3}^*/p_y	32	π_{H-1}	π_{L+9}^*	18	π_{H-1}	π_{L+3}^*/p_y
	28	π_{H-1}	π_{L+9}^*/p_y				17	π_{H-1}	π_{L+9}^*/p_y
1^3A_2	89	π_H	$3s$	54	π_H	$3s$	67	π_H	$3s$
				17	π_H	$3p_z$			
1^3B_2	89	π_H	$3p_x$	65	π_H	$3p_x$	69	π_H	$3p_x$
		π_{H-1}	Ry_{L+1}	6	π_H	$3d_{xz}$	5	π_{H-1}	$3s$
π_{L+3}^*/p_y and π_{L+9}^*/p_y BH-LYP orbitals arise from combination of π_{L+9}^* and p_y orbitals. In HF and CASSCF calculations this orbitals do not mix.									

Table S25.: Calculated percentage of electron configurations in the discussed wave functions of **furan** obtained at the DFT/MRCI-R, and CASPT2 (6,9) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

DFT/MRCI-R				CASPT2 (6,9)		
State	%	Excitation		%	Excitation	
		from	to		from	to
2 ¹ A ₁	33	π_H	π_{L+10}^*	38	π_{H-1}	π_{L+9}^*
	28	π_{H-1}	π_{L+3}^*/p_y	31	π_H	π_{L+10}^*
	22	π_{H-1}	π_{L+9}^*/p_y	8	π_H^2	π_{L+9}^*
				7	π_H, π_{H-1}	$\pi_{L+9}^*, \pi_{L+10}^*$
1 ¹ B ₁	73	π_H	π_{L+3}^*/p_y	78	π_H	π_{L+9}^*
	23	π_H	π_{L+9}^*/p_y	9	π_H	p_y
1 ¹ A ₂	91	π_H	3s	91	π_H	3s
1 ¹ B ₂	92	π_H	3p _x	90	π_H	3p _x
1 ³ B ₁	47	π_H	π_{L+3}^*/p_y	85	π_H	π_{L+9}^*
	46	π_H	π_{L+9}^*/p_y	7	π_{H-1}	π_{L+10}^*
1 ³ A ₁	39	π_H	π_{L+10}^*	44	π_H	π_{L+10}^*
	29	π_{H-1}	π_{L+3}^*/p_y	45	π_{H-1}	π_{L+9}^*
	26	π_{H-1}	π_{L+9}^*/p_y			
1 ³ A ₂	90	π_H	3s	91	π_H	3s
1 ³ B ₂	90	π_H	3p _x	88	π_H	3p _x
				5 π_{H-1}		3s
π_{L+3}^*/p_y and π_{L+9}^*/p_y BH-LYP orbitals arise from combination of π_{L+9}^* and p_y orbitals. In HF and CASSCF calculations these orbitals do not mix.						

S4.5. Thiophene

Table S26. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of **thiophene** using the valence basis. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
2^1A_1	$\pi \rightarrow \pi^*$	5.55 (0.095)	5.54 (0.109)	5.27 (0.030)	5.23 (0.057)	5.43^a
1^1B_1	$\pi \rightarrow \pi^*$	5.81 (0.109)	5.75 (0.120)	5.75 (0.074)	5.74 (0.078)	5.61^a
1^1B_2	$\pi \rightarrow \sigma^*$	6.06 (0)	6.13 (0)	6.23 (0.001)	6.16 (0.001)	
1^1A_2	$\pi \rightarrow \sigma^*$	6.28 (0)	6.31 (0)	6.27 (0)	6.17 (0)	
3^1A_1	$\pi \rightarrow \pi^*$	7.29 (0.321)	7.35 (0.400)	6.97 (0.173)	6.83 (0.223)	7.05^b
1^3B_1	$\pi \rightarrow \pi^*$	3.78	3.78	3.71	3.74	3.75^c, 3.80^d
1^3A_1	$\pi \rightarrow \pi^*$	4.58	4.56	4.48	4.46	4.62^c, 4.70^d
1^3B_2	$\pi \rightarrow \sigma^*$	5.86	5.91	6.00	5.92	
2^3A_1	$\pi \rightarrow \pi^*$	5.92	5.94	5.77	5.72	
1^3A_2	$\pi \rightarrow \sigma^*$	5.95	6.01	5.95	5.90	

^a Electron energy-loss maximum (gas) [11]

^b VUV absorption maximum (gas) [15]

^c Electron impact maximum (gas) [12]

^d Electron energy-loss maximum (gas) [15]

Table S27. Calculated percentage of electron configurations in the excited states wave functions of **thiophene** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	%	Excitation		%	Excitation		%	Excitation	
		from	to		from	to		from	to
2^1A_1	74	π_{H-1}	π_L^*	47	π_{H-1}	π_L^*	45	π_{H-1}	π_L^*
	15	π_H	π_{L+3}^*	16	π_H	π_{L+3}^*	17	π_H	π_{L+3}^*
	3	π_{H-1}, π_H	π_L^*, π_{L+3}^*	3	π_{H-1}, π_H	π_L^*, π_{L+3}^*	3	π_{H-1}, π_H	π_L^*, π_{L+3}^*
	2	π_{H-3}, π_{H-1}	π_L^*, π_L^*	3	π_{H-3}, π_{H-1}	π_L^*, π_L^*	3	π_{H-3}, π_{H-1}	π_L^*, π_L^*
1^1B_1	89	π_H	π_L^*	66	π_H	π_L^*	66	π_H	π_L^*
	2	π_{H-1}	π_{L+3}^*	2	π_{H-1}	π_{L+3}^*	2	π_{H-3}, π_H	π_L^*, π_L^*
	2	π_{H-1}, π_H	π_L^*, π_L^*	2	π_{H-1}, π_H	π_L^*, π_L^*	2	n_{H-2}	σ_{L+1}^*
	2	n_{H-2}	σ_{L+1}^*	2	π_{H-3}, π_H	π_L^*, π_L^*			
1^1B_2	85	π_H	σ_{L+1}^*	54	π_H	σ_{L+1}^*	64	π_H	σ_{L+1}^*
	5	π_{H-1}, π_H	π_L^*, σ_{L+1}^*	8	π_H	σ_{L+7}^*	6	π_{H-1}, π_H	π_L^*, σ_{L+1}^*
	2	π_H	σ_{L+7}^*	6	π_H	Ry_{L+5}	2	π_{H-3}, π_H	π_L^*, σ_{L+1}^*
	2	π_H	Ry_{L+5}	5	π_{H-1}, π_H	π_L^*, σ_{L+1}^*			
1^1A_2	87	π_{H-1}	σ_{L+1}^*	57	π_{H-1}	σ_{L+1}^*	67	π_{H-1}	σ_{L+1}^*
	3	π_{H-1}	σ_{L+7}^*	9	π_{H-1}	σ_{L+7}^*	2	π_{H-1}, π_H	$\sigma_{L+1}^*, \pi_{L+3}^*$
	2	π_{H-1}	Ry_{L+5}	5	π_{H-1}	Ry_{L+5}			
3^1A_1	46	π_H	π_{L+3}^*	18	π_H	π_{L+3}^*	17	π_{H-1}	π_L^*
	15	π_{H-3}	π_L^*	16	π_{H-3}	π_L^*	16	π_H	π_{L+3}^*
	13	π_{H-1}	π_L^*	15	π_{H-1}	π_L^*	15	π_{H-3}	π_L^*
	12	π_H, π_H	π_L^*, π_L^*	14	π_H, π_H	π_L^*, π_L^*	14	π_H, π_H	π_L^*, π_L^*
	2	π_{H-1}, π_{H-1}	π_L^*, π_L^*	3	π_{H-1}, π_{H-1}	π_L^*, π_L^*	4	π_{H-1}, π_{H-1}	π_L^*, π_L^*
	2	π_H, π_H	π_{L+3}, π_{L+3}^*	2	π_H, π_H	π_{L+3}, π_{L+3}^*	2	π_H, π_H	π_{L+3}, π_{L+3}^*
	2	σ_{H-4}	σ_{L+1}^*				2	σ_{H-4}	σ_{L+1}^*
1^3B_1	93	π_H	π_L^*	70	π_H	π_L^*	69	π_H	π_L^*
	2	π_{H-1}	π_{L+3}^*	2	π_{H-3}	π_{L+3}^*	3	π_{H-1}	π_{L+3}^*
	2	π_{H-3}	π_{L+3}^*	2	π_{H-1}	π_{L+3}^*	2	π_{H-3}	π_{L+3}^*
1^3A_1	87	π_{H-1}	π_L^*	54	π_{H-1}	π_L^*	54	π_{H-1}	π_L^*
	9	π_H	π_{L+3}^*	17	π_H	π_{L+3}^*	16	π_H	π_{L+3}^*
				2	π_{H-3}	π_L^*	2	π_{H-3}	π_L^*
							2	π_{H-1}, π_H	π_L^*, π_{L+3}^*
1^3B_2	88	π_H	σ_{L+1}^*	53	π_H	σ_{L+1}^*	65	π_H	σ_{L+1}^*
	4	π_{H-1}, π_H	π_L^*, σ_{L+1}^*	9	π_H	σ_{L+7}^*	5	π_{H-1}, π_H	π_L^*, σ_{L+1}^*
	2	π_H	σ_{L+7}^*	5	π_H	Ry_{L+5}			
	2	π_H	Ry_{L+5}	5	π_{H-1}, π_H	π_L^*, σ_{L+1}^*			
2^3A_1	74	π_H	π_{L+3}^*	42	π_H	π_{L+3}^*	45	π_H	π_{L+3}^*
	11	π_{H-3}	π_L^*	21	π_{H-1}	π_L^*	20	π_{H-1}	π_L^*
	10	π_{H-1}	π_L^*	9	π_{H-3}	π_L^*	9	π_{H-3}	π_L^*
1^3A_2	86	π_{H-1}	σ_{L+1}^*	53	π_{H-1}	σ_{L+1}^*	66	π_{H-1}	σ_{L+1}^*
	3	π_{H-1}	σ_{L+7}^*	11	π_{H-1}	σ_{L+7}^*	3	π_{H-3}	σ_{L+1}^*
	3	π_{H-1}	Ry_{L+5}	6	π_{H-1}	Ry_{L+5}			
	3	π_{H-3}	σ_{L+1}^*	2	π_{H-3}	σ_{L+1}^*			

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:

The σ_{L+1}^* bh-lyp orbital corresponds to the σ_{L+2}^* hf orbital;

Table S28. Selected matrix elements (cm^{-1}) for **thiophene** calculated with DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) methods using the valence basis.

	SOMEs(cm^{-1})			
	DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 1^1A_1 \rangle$	127.7	125.7	109.1	113.5
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 2^1A_1 \rangle$	55.6	56.0	39.9	41.0
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 3^1A_1 \rangle$	29.6	28.0	29.3	36.7
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } y} 1^1A_1 \rangle$	0.1	0.3	0.6	0.4
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } x} 1^1A_1 \rangle$	6.9	6.4	6.1	6.5
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } x} 2^1A_1 \rangle$	1.8	2.2	3.3	3.9
$\langle 1^3A_1 \hat{\mathcal{H}}_{\text{SO } z} 1^1A_2 \rangle$	47.1	45.9	32.5	36.1
$\langle 1^3A_1 \hat{\mathcal{H}}_{\text{SO } y} 1^1B_1 \rangle$	0.5	0.4	0.4	0.4
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } x} 1^1B_1 \rangle$	17.6	17.2	15.5	15.7
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } z} 1^1B_2 \rangle$	65.0	64.0	49.5	57.5
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 1^3A_1 \rangle$	41.2	41.0	27.9	29.4
$\langle 1^3A_2 \hat{\mathcal{H}}_{\text{SO } z} 2^3A_1 \rangle$	13.2	11.5	18.3	17.3
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } y} 1^3A_1 \rangle$	0.2	0.2	0.1	0.0
$\langle 1^3B_1 \hat{\mathcal{H}}_{\text{SO } x} 1^3A_2 \rangle$	3.0	2.5	3.2	3.7
$\langle 1^3B_2 \hat{\mathcal{H}}_{\text{SO } z} 1^3B_1 \rangle$	64.7	66.6	53.9	60.1

Table S29. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF), MR-MP2(BH-LYP) and CASPT2 (6,10) vertical excitation energies of **thiophene** using the augmented basis. The CASPT2 active space consists of following occupied/unoccupied orbitals: $0/2\ a_1$, $0/2\ b_1$, $2/2\ b_2$ and $1/1\ a_2$. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)					Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	CASPT2 (6,10)	
2^1A_1	$\pi \rightarrow \pi^*$	5.43 (0.114)	5.43 (0.124)	5.23 (0.270)	5.18 (0.063)	5.47 (0.080)	5.43^a
1^1B_1	$\pi \rightarrow \pi^*$	5.65 (0.102)	5.62 (0.115)	6.14 (0.086)	5.62 (0.042)	5.47 (0.124)	5.61^a
1^1B_2	$\pi \rightarrow \sigma^*/4p_x$	5.83 (0.004)	5.88 (0.005)	6.29 (0.016)	6.21 (0.014)	6.28 (0.015)	
1^1A_2	$\pi \rightarrow 4s$	5.85 (0)	5.84 (0)	6.11 (0)	6.16 (0)	6.03 (0)	5.93^c
2^1A_2	$\pi \rightarrow \sigma^*/4p_x$	6.06 (0)	6.10 (0)	6.25 (0)	6.21 (0)	6.33 (0)	
:							
3^1A_1	$\pi \rightarrow \pi^*$	7.08 (0.167)	7.02 (0.114)	7.04 (0.150)	6.89 (0.158)	6.99 (0.332)	7.05^b
1^3B_1	$\pi \rightarrow \pi^*$	3.62	3.71	3.73	3.75	3.75	3.75^c, 3.80^d
1^3A_1	$\pi \rightarrow \pi^*$	4.45	4.50	4.53	4.47	4.59	4.62^c, 4.70^d
1^3B_2	$\pi \rightarrow \sigma^*/4p_x$	5.64	5.71	6.07	6.04	6.11	
1^3A_2	$\pi \rightarrow 4s$	5.77	5.78	6.09 ¹	6.09 ¹	6.00	
2^3A_2	$\pi \rightarrow \sigma^*/4p_x$	5.79	5.86	5.95 ²	5.88 ²	5.99	
2^3A_1	$\pi \rightarrow \pi^*$	5.88	5.92	5.78	5.70	5.68	
MR-MP2(HF): $1^1 2^3A_2$, $2^1 1^3A_2$							
MR-MP2(BH-LYP): $1^1 2^3A_2$, $2^1 1^3A_2$							
^a Electron energy-loss maximum (gas) [11]							
^b VUV absorption maximum (gas) [15]							
^c Electron impact maximum (gas) [12]							
^d Electron energy-loss maximum (gas) [15]							

Table S30. Calculated percentage of electron configurations in the excited states wave functions of **thiophene** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	%	Excitation		%	Excitation		%	Excitation	
		from	to		from	to		from	to
2^1A_1	55	π_{H-1}	π_{L+4}^*	46	π_{H-1}	π_{L+4}^*	36	π_{H-1}	π_{L+4}^*
	21	π_{H-1}	$4p_y$	16	π_H	π_{L+11}^*	16	π_H	π_{L+11}^*
	13	π_H	π_{L+11}^*				9	π_{H-1}	$4p_y$
1^1B_1	66	π_H	π_{L+4}^*	44	π_H	π_{L+4}^*	39	π_H	π_{L+4}^*
	24	π_H	$4p_y$	20	π_H	$4p_y$	24	π_H	$4p_y$
1^1B_2	47	π_H	σ_{L+10}^*	53	π_H	$4p_x$	50	π_H	$4p_x$
	36	π_H	$4p_x$	16	π_H	σ_{L+10}^*	13	π_{H-1}	$4s$
	8	π_H	$3d_{xz}$				8	π_H	σ_{L+10}^*
2^1A_2	54	π_{H-1}	σ_{L+10}^*	34	π_{H-1}	σ_{L+10}^*	39	π_{H-1}	$4p_x$
	28	π_{H-1}	$4p_x$	27	π_{H-1}	$4p_x$	27	π_{H-1}	σ_{L+10}^*
	11	π_{H-1}	$3d_{xz}$	6	π_H	$4s$			
3^1A_1	55	π_{H-1}	$4p_y$	18	π_{H-1}	$3d_{yz}$	27	π_H	$3d_{xy}$
	19	π_H	π_{L+11}^*	12	π_{H-3}	π_{L+4}^*	10	π_{H-1}	π_{L+4}^*
				12	π_H	π_{L+11}^*	9	π_H	π_{L+11}^*
				10	π_H^2	π_{L+4}^{2*}	7	π_{H-3}	π_{L+4}^{2*}
							5	π_H^2	π_{L+4}^{2*}
1^3B_1	72	π_H	π_{L+4}^*	69	π_H	π_{L+4}^*	57	π_H	π_{L+4}^*
	21	π_H	$4p_y$				14	π_H	$4p_y$
1^3A_1	70	π_{H-1}	π_{L+4}^*	53	π_{H-1}	π_{L+4}^*	44	π_{H-1}	π_{L+4}^*
	19	π_{H-1}	$4p_y$	17	π_H	π_{L+11}^*	17	π_H	π_{L+11}^*
	7	π_H	π_{L+11}^*				10	π_{H-1}	$4p_y$
1^3B_2	54	π_H	σ_{L+10}^*	42	π_H	$4p_x$	49	π_H	$4p_x$
	29	π_H	$4p_x$	28	π_H	σ_{L+10}^*	19	π_H	σ_{L+10}^*
	9	π_H	$3d_{xz}$						
2^3A_2	46	π_{H-1}	σ_{L+10}^*	48	π_{H-1}	σ_{L+10}^*	42	π_{H-1}	σ_{L+10}^*
	22	π_H	$4s$	17	π_{H-1}	$4p_x$	24	π_{H-1}	$4p_x$
	17	π_{H-1}	$4p_x$						
	7	π_{H-1}	$3d_{xz}$						
2^3A_1	73	π_H	π_{L+11}^*	41	π_H	π_{L+11}^*	43	π_H	π_{L+11}^*
	10	π_{H-3}	π_{L+4}^*	21	π_{H-1}	π_{L+4}^*	17	π_{H-1}	π_{L+4}^*
	6	π_{H-1}	π_{L+4}^*	10	π_{H-3}	π_{L+4}^*	7	π_{H-3}	π_{L+4}^*

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:

The π_{L+4}^* bh-lyp orbital corresponds to the π_{L+9}^* hf orbital;

Table S31.: Calculated percentage of electron configurations in the discussed wave functions of **thiophene** obtained at the DFT/MRCI-R, and CASPT2 (6,10) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

State	DFT/MRCI-R			CASPT2 (6,10)		
	%	Excitation		%	Excitation	
		from	to		from	to
2^1A_1	56	π_{H-1}	π_{L+4}^*	46	π_{H-1}	π_{L+4}^*
	20	π_{H-1}	$4p_y$	19	π_H	π_{L+11}^*
	13	π_H	π_{L+11}^*	10	π_{H-1}	$4p_y$
1^1B_1	69	π_H	π_{L+4}^*	82	π_H	π_{L+4}^*
	22	π_H	$4p_y$	7	π_{H-1}	π_{L+11}^*
1^1B_2	44	π_H	σ_{L+10}^*	78	π_H	σ^*/p_x
	40	π_H	$4p_x$	5	π_H	$4p_x$
	7	π_H	$3d_{xz}$			
2^1A_2	53	π_{H-1}	σ_{L+10}^*	85	π_{H-1}	σ^*/p_x
	30	π_{H-1}	$4p_x$			
	11	π_{H-1}	$3d_{xz}$			
3^1A_1	66	π_{H-1}	$4p_y$	25	π_{H-1}	π_{L+4}^*
	11	π_H	π_{L+11}^*	25	π_H^2	π_{L+4}^*
	9	π_{H-1}	π_{L+4}^*	21	π_{H-3}	π_{L+4}^*
				9	π_H	π_{L+11}^*
				7	π_{H-1}^2	π_{L+4}^*
1^3B_1	74	π_H	π_{L+4}^*	87	π_H	π_{L+4}^*
	20	π_H	$4p_y$			
1^3A_1	71	π_{H-1}	π_{L+4}^*	60	π_{H-1}	π_{L+4}^*
	17	π_{H-1}	$4p_y$	25	π_H	π_{L+11}^*
	7	π_H	π_{L+11}^*			
1^3B_2	51	π_H	σ_{L+10}^*	79	π_H	σ^*/p_x
	32	π_H	$4p_x$	7	π_{H-1}	$4s$
	9	π_H	$3d_{xz}$			
2^3A_2	59	π_{H-1}	σ_{L+10}^*	77	π_{H-1}	σ^*/p_x
	23	π_{H-1}	$4p_x$	7	π_{H-1}	σ^*/p_x
	10	π_{H-1}	$3d_{xz}$			
2^3A_1	75	π_H	π_{L+11}^*	43	π_H	π_{L+11}^*
	8	π_{H-3}	π_{L+4}^*	35	π_{H-1}	π_{L+4}^*
	6	π_{H-1}	π_{L+4}^*	18	π_{H-3}	π_{L+4}^*
<p>The σ^*/p_x and σ^*/p_x CASSCF orbitals are, respectively, positive and negative linear combinations of σ^* and p_x orbitals. In HF and DFT calculations these orbitals do not mix.</p>						

S4.6. Quinoxaline

Table S32. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of **quinoxaline**. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
1^1B_1	$n \rightarrow \pi^*$	3.54 (0.007)	3.63 (0.008)	3.24 (0.004)	3.24 (0.005)	3.96^a
2^1A_1	$\pi \rightarrow \pi^*$	4.14 (0.080)	4.13 (0.094)	3.75 (0.060)	3.61 (0.064)	
1^1B_2	$\pi \rightarrow \pi^*$	4.36 (0.052)	4.33 (0.059)	4.68 (0.033)	4.57 (0.025)	
1^1A_2	$n \rightarrow \pi^*$	4.75 (0)	4.93 (0)	4.68 (0) ¹	4.56 (0) ¹	
2^1A_2	$n \rightarrow \pi^*$	5.05 (0)	5.14 (0)	4.47 (0) ²	4.28 (0) ²	
1^3B_2	$\pi \rightarrow \pi^*$	3.06	3.02	3.00	2.88	
1^3B_1	$n \rightarrow \pi^*$	3.16	3.25	2.83	2.74	
1^3A_1	$\pi \rightarrow \pi^*$	3.70	3.63	3.72	3.59	
1^3A_2	$n \rightarrow \pi^*$	4.42	4.57	4.32	4.17 ³	
2^3B_2	$\pi \rightarrow \pi^*$	4.53	4.41	4.22	4.10	

MRMP2(HF): 1^2A_2 , 2^1A_2

MRMP2(BHLYP): 1^2A_2 , 2^1A_2 , 3^2A_2

^a Vapor absorption maximum [16]

Table S33.: Calculated percentage of electron configurations in the excited states wave functions of **quinoxaline** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	%	Excitation		%	Excitation		%	Excitation	
		from	to		from	to		from	to
1^1B_1	83	n_{H-2}	π_L^*	53	n_{H-2}	π_L^*	53	n_{H-2}	π_L^*
	5	n_{H-2}	π_{L+2}^*	5	n_{H-2}	π_{L+2}^*	4	n_{H-2}	π_{L+2}^*
	2	n_{H-3}, π_H	π_L^*, π_L^*				2	n_{H-3}, π_{H-4}	π_L^*, π_L^*
2^1A_1	63	π_{H-1}	π_L^*	41	π_{H-1}	π_L^*	40	π_{H-1}	π_L^*
	24	π_H	π_{L+1}^*	16	π_H	π_{L+1}^*	15	π_H	π_{L+1}^*
1^1B_2	83	π_H	π_L^*	53	π_H	π_L^*	51	π_H	π_L^*
	2	π_{H-1}, π_H	π_L^*, π_L^*	4	π_{H-1}	π_{L+1}^*	3	π_{H-1}, π_H	π_L^*, π_L^*
	2	π_{H-1}	π_{L+1}^*	3	π_{H-1}, π_H	π_L^*, π_L^*	3	π_{H-1}	π_{L+1}^*
	2	π_H	π_{L+2}^*				2	π_H	π_{L+2}^*
1^1A_2	61	n_{H-3}	π_L^*	43	n_{H-3}	π_L^*	40	n_{H-3}	π_L^*
	11	n_{H-2}	π_{L+1}^*	4	n_{H-3}	π_{L+2}^*	6	n_{H-2}, π_H	π_L^*, π_L^*
	8	n_{H-2}, π_H	π_L^*, π_L^*	4	n_{H-2}	π_{L+1}^*	4	n_{H-2}	π_{L+1}^*
	4	n_{H-3}	π_{L+2}^*	4	n_{H-2}, π_H	π_L^*, π_L^*	3	n_{H-3}	π_{L+2}^*
	3	n_{H-2}	π_{L+5}^*	2	π_{H-4}, n_{H-2}	π_L^*, π_L^*	2	π_{H-4}, n_{H-2}	π_L^*, π_L^*
	3	π_{H-4}, n_{H-2}	π_L^*, π_L^*	2	n_{H-2}	π_{L+5}^*	2	n_{H-2}	π_{L+5}^*
2^1A_2	73	n_{H-2}	π_{L+1}^*	51	n_{H-2}	π_{L+1}^*	50	n_{H-2}	π_{L+1}^*
	8	n_{H-3}	π_L^*	3	n_{H-3}	π_L^*	3	n_{H-3}	π_L^*
	3	n_{H-2}, π_H	π_L^*, π_L^*	2	n_{H-2}, π_{H-1}	π_L^*, π_{L+1}^*	2	n_{H-2}, π_{H-1}	π_L^*, π_{L+1}^*
	3	n_{H-2}, π_{H-1}	π_L^*, π_{L+1}^*						
1^3B_2	83	π_H	π_L^*	52	π_H	π_L^*	50	π_H	π_L^*
	3	π_H	π_{L+2}^*	3	π_{H-1}	π_{L+1}^*	3	π_{H-1}	π_{L+1}^*
	3	π_{H-1}	π_{L+1}^*	3	π_H	π_{L+2}^*	3	π_H	π_{L+2}^*
	2	π_{H-4}	π_{L+2}^*	2	π_{H-4}	π_{L+2}^*	2	π_{H-4}	π_{L+2}^*
	2	π_{H-4}	π_L^*				2	π_{H-4}	π_L^*
1^3B_1	82	n_{H-2}	π_L^*	52	n_{H-2}	π_L^*	52	n_{H-2}	π_L^*
	8	n_{H-2}	π_{L+2}^*	6	n_{H-2}	π_{L+2}^*	5	n_{H-2}	π_{L+2}^*
	2	n_{H-3}	π_{L+5}^*	2	n_{H-3}	π_{L+5}^*	2	n_{H-3}	π_{L+5}^*
1^3A_1	85	π_{H-1}	π_L^*	54	π_{H-1}	π_L^*	52	π_{H-1}	π_L^*
	6	π_H	π_{L+1}^*	7	π_H	π_{L+1}^*	7	π_H	π_{L+1}^*
1^3A_2	69	n_{H-3}	π_L^*	45	n_{H-3}	π_L^*	44	n_{H-3}	π_L^*
	8	n_{H-3}	π_{L+2}^*	7	n_{H-3}	π_{L+2}^*	6	n_{H-3}	π_{L+2}^*
	6	n_{H-2}	π_{L+1}^*	4	n_{H-2}	π_{L+5}^*	4	n_{H-2}	π_{L+5}^*
	6	n_{H-2}	π_{L+5}^*	2	n_{H-2}	π_{L+1}^*	2	n_{H-2}, π_H	π_L^*, π_L^*
	2	n_{H-2}, π_H	π_L^*, π_L^*				2	n_{H-2}	π_{L+1}^*

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:

The n_{H-3} bh-lyp orbital corresponds to the n_{H-5} hf orbital;

The π_{H-4} bh-lyp orbital corresponds to the π_{H-3} hf orbital;

The π_{L+5}^* bh-lyp orbital corresponds to the π_{L+9}^* hf orbital;

S4.7. *Quinazoline*

Table S34. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF), MR-MP2(BH-LYP) vertical excitation energies of **quinazoline**. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
$1^1A''$	$n \rightarrow \pi^*$	3.80 (0.007)	3.92 (0.008)	3.49 (0.004)	3.39 (0.004)	
$2^1A'$	$\pi \rightarrow \pi^*$	4.27 (0.032)	4.26 (0.040)	3.90 (0.019)	3.55 (0.018)	4.07^a
$3^1A'$	$\pi \rightarrow \pi^*$	4.72 (0.063)	4.68 (0.067)	4.86 (0.049)	4.62 (0.034)	4.66^a
$2^1A''$	$n \rightarrow \pi^*$	4.76 (0)	4.89 (0)	4.35 (0)	4.13 (0)	
$3^1A''$	$n \rightarrow \pi^*$	5.18 (0.001)	5.29 (0.001)	4.72 (0)	4.42 (0)	
$1^3A'$	$\pi \rightarrow \pi^*$	3.16	3.13	3.13	2.96	
$1^3A''$	$n \rightarrow \pi^*$	3.54	3.66	3.16	3.10	
$2^3A'$	$\pi \rightarrow \pi^*$	4.06	4.00	3.91	3.72	
$3^3A'$	$\pi \rightarrow \pi^*$	4.38	4.33	4.50 ¹	4.27 ¹	
$2^3A''$	$n \rightarrow \pi^*$	4.44	4.58	4.03	3.75	

MRMP2(HF):¹4³A'

MRMP2(BHLYP):¹4³A'

^a Absorption maximum in cyclohexane and etylether [17]

Table S35.: Calculated percentage of electron configurations in the excited states wave functions of **quinazoline** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	Excitation			Excitation			Excitation		
	%	from	to	%	from	to	%	from	to
$1^1A''$	81	n_{H-2}	π_L^*	53	n_{H-2}	π_L^*	52	n_{H-2}	π_L^*
	6	n_{H-2}	π_{L+2}^*	5	n_{H-2}	π_{L+2}^*	4	n_{H-2}	π_{L+2}^*
$3^1A'$	52	π_H	π_L^*	32	π_H	π_L^*	38	π_H	π_L^*
	23	π_{H-1}	π_L^*	17	π_{H-1}	π_L^*	11	π_{H-1}	π_L^*
	12	π_H	π_{L+1}^*	9	π_H	π_{L+1}^*	5	π_H	π_{L+1}^*
				2	π_{H-1}	π_{L+1}^*	3	π_{H-1}	π_{L+1}^*
$2^1A''$	68	n_{H-2}	π_{L+1}^*	45	n_{H-2}	π_{L+1}^*	42	n_{H-2}	π_{L+1}^*
	13	n_{H-3}	π_L^*	9	n_{H-3}	π_L^*	10	n_{H-3}	π_L^*
	4	n_{H-2}	π_{L+5}^*	3	n_{H-2}	π_{L+5}^*	3	n_{H-2}	π_{L+5}^*
$3^1A''$	64	n_{H-3}	π_L^*	42	n_{H-3}	π_L^*	39	n_{H-3}	π_L^*
	15	n_{H-2}	π_{L+1}^*	11	n_{H-2}	π_{L+1}^*	12	n_{H-2}	π_{L+1}^*
	4	n_{H-3}	π_{L+2}^*	3	n_{H-3}	π_{L+2}^*	3	n_{H-3}	π_{L+2}^*
	2	n_{H-2}, π_{H-1}	π_L^*, π_{L+1}^*				2	n_{H-2}, π_{H-1}	π_L^*, π_{L+1}^*
$1^3A'$	81	π_H	π_L^*	52	π_H	π_L^*	53	π_H	π_L^*
	3	π_{H-4}	π_{L+2}^*	4	π_{H-1}	π_L^*	2	π_{H-4}	π_{L+2}^*
	3	π_{H-1}	π_L^*	2	π_{H-4}	π_{L+2}^*	2	π_H	π_{L+2}^*
	2	π_H	π_{L+1}^*	2	π_H	π_{L+1}^*	2	π_{H-1}	π_L^*
	2	π_{H-1}	π_{L+1}^*	2	π_H	π_{L+2}^*			
$1^3A''$	80	n_{H-2}	π_L^*	51	n_{H-2}	π_L^*	51	n_{H-2}	π_L^*
	8	n_{H-2}	π_{L+2}^*	6	n_{H-2}	π_{L+2}^*	5	n_{H-2}	π_{L+2}^*
	2	n_{H-3}	π_{L+5}^*						
$2^3A''$	49	n_{H-2}	π_{L+1}^*	25	n_{H-2}	π_{L+1}^*	24	n_{H-3}	π_L^*
	27	n_{H-3}	π_L^*	21	n_{H-3}	π_L^*	22	n_{H-2}	π_{L+1}^*
	8	n_{H-2}	π_{L+5}^*	7	n_{H-2}	π_{L+5}^*	7	n_{H-2}	π_{L+5}^*
	3	n_{H-3}	π_{L+2}^*	3	n_{H-3}	π_{L+2}^*	3	n_{H-3}	π_{L+2}^*

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:

The n_{H-3} bh-lyp orbital corresponds to the n_{H-4} hf orbital;

The π_{H-4} bh-lyp orbital corresponds to the π_{H-3} hf orbital;

The π_{L+5}^* bh-lyp orbital corresponds to the π_{L+10}^* hf orbital;

S4.8. *Pyranthione*

Table S36. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of **pyranthione**. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
1^1A_2	$n \rightarrow \pi^*$	2.16 (0)	2.22 (0)	2.26 (0)	2.25 (0)	2.25^a
1^1B_2	$n \rightarrow \pi^*$	3.76 (0)	3.66 (0)	3.95 (0.001)	3.85 (0)	
2^1A_1	$\pi \rightarrow \pi^*$	3.92 (0.497)	3.90 (0.544)	3.76 (0.495)	3.71 (0.482)	3.78^a
1^1B_1	$\pi \rightarrow \pi^*$	4.32 (0.003)	4.35 (0.002)	4.39 (0.001)	4.30 (0.002)	
2^1B_1	$\pi \rightarrow \pi^*$	5.59 (0.107)	5.63 (0.121)	5.54 (0.082)	5.37 (0.067)	
1^3A_2	$n \rightarrow \pi^*$	2.05	2.08	2.15	2.16	
1^3A_1	$\pi \rightarrow \pi^*$	2.28	2.19	2.22	2.19	
1^3B_1	$\pi \rightarrow \pi^*$	3.70	3.71	3.57	3.49	
1^3B_2	$n \rightarrow \pi^*$	3.80	3.61	3.94	3.83	
2^3A_1	$\pi \rightarrow \pi^*$	4.85	4.82	4.74	4.66	

^a Absorption maximum in 3-methylpentane [18]

Table S37.: Calculated percentage of electron configurations in the excited states wave functions of **pyranthione** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	%	Excitation		%	Excitation		%	Excitation	
		from	to		from	to		from	to
1^1A_2	87	n_H	π_L^*	62	n_H	π_L^*	60	n_H	π_L^*
	6	π_{H-1}, n_H	π_L^*, π_L^*	6	π_{H-1}, n_H	π_L^*, π_L^*	7	π_{H-1}, n_H	π_L^*, π_L^*
	2	π_{H-2}, n_H	π_L^*, π_{L+1}^*						
1^1B_2	76	n_H	π_{L+1}^*	50	n_H	π_{L+1}^*	48	n_H	π_{L+1}^*
	12	π_{H-1}, n_H	π_L^*, π_{L+1}^*	13	π_{H-1}, n_H	π_L^*, π_{L+1}^*	13	π_{H-1}, n_H	π_L^*, π_{L+1}^*
	5	π_{H-2}, n_H	π_L^*, π_{L+1}^*	4	π_{H-2}, n_H	π_L^*, π_L^*	5	π_{H-2}, n_H	π_L^*, π_L^*
2^1A_1	81	π_{H-1}	π_L^*	55	π_{H-1}	π_L^*	53	π_{H-1}	π_L^*
	6	π_{H-1}, π_{H-1}	π_L^*, π_L^*	6	π_{H-1}, π_{H-1}	π_L^*, π_L^*	6	π_{H-1}, π_{H-1}	π_L^*, π_L^*
	4	π_{H-2}, π_{H-1}	π_L^*, π_{L+1}^*	2	π_{H-2}, π_{H-1}	π_L^*, π_{L+1}^*	3	π_{H-2}, π_{H-1}	π_L^*, π_{L+1}^*
							2	π_{H-3}, π_{H-1}	π_L^*, π_L^*
1^1B_1	77	π_{H-1}	π_{L+1}^*	51	π_{H-1}	π_{L+1}^*	48	π_{H-1}	π_{L+1}^*
	10	π_{H-1}, π_{H-1}	π_L^*, π_{L+1}^*	9	π_{H-1}, π_{H-1}	π_L^*, π_{L+1}^*	11	π_{H-1}, π_{H-1}	π_L^*, π_{L+1}^*
	3	π_{H-2}, π_{H-1}	π_L^*, π_L^*	3	π_{H-2}, π_{H-1}	π_L^*, π_L^*	3	π_{H-2}, π_{H-1}	π_L^*, π_L^*
	2	π_{H-3}, π_{H-1}	π_L^*, π_{L+1}^*	2	π_{H-3}, π_{H-1}	π_L^*, π_{L+1}^*	3	π_{H-2}	π_L^*
1^3A_2	91	n_H	π_L^*	63	n_H	π_L^*	61	n_H	π_L^*
	3	π_{H-1}, n_H	π_L^*, π_L^*	5	π_{H-1}, n_H	π_L^*, π_L^*	5	π_{H-1}, n_H	π_L^*, π_L^*
1^3A_1	94	π_{H-1}	π_L^*	66	π_{H-1}	π_L^*	65	π_{H-1}	π_L^*
				2	π_{H-2}	π_{L+1}^*	2	π_{H-2}	π_{L+1}^*
1^3B_1	71	π_{H-1}	π_{L+1}^*	40	π_{H-1}	π_{L+1}^*	42	π_{H-1}	π_{L+1}^*
	16	π_{H-2}	π_L^*	20	π_{H-2}	π_L^*	16	π_{H-2}	π_L^*
	2	π_{H-2}	π_{L+6}^*	4	π_{H-3}	π_{L+1}^*	3	π_{H-2}	π_{L+6}^*
	2	π_{H-3}	π_{L+1}^*	3	π_{H-2}	π_{L+6}^*	3	π_{H-3}	π_{L+1}^*
	2	π_{H-1}, π_{H-1}	π_L^*, π_{L+1}^*	2	π_{H-1}, π_{H-1}	π_L^*, π_{L+1}^*	2	π_{H-1}, π_{H-1}	π_L^*, π_{L+1}^*
1^3B_2	81	n_H	π_{L+1}^*	51	n_H	π_{L+1}^*	49	n_H	π_{L+1}^*
	10	π_{H-1}, n_H	π_L^*, π_{L+1}^*	13	π_{H-1}, n_H	π_L^*, π_{L+1}^*	13	π_{H-1}, n_H	π_L^*, π_{L+1}^*
	3	π_{H-2}, n_H	π_L^*, π_L^*	4	π_{H-2}, n_H	π_L^*, π_L^*	5	π_{H-2}, n_H	π_L^*, π_L^*
2^3A_1	63	π_{H-2}	π_{L+1}^*	43	π_{H-2}	π_{L+1}^*	42	π_{H-2}	π_{L+1}^*
	18	π_{H-3}	π_L^*	15	π_{H-3}	π_L^*	15	π_{H-3}	π_L^*
	11	π_{H-1}	π_{L+6}^*	7	π_{H-1}	π_{L+6}^*	7	π_{H-1}	π_{L+6}^*
	2	π_{H-2}, π_{H-1}	π_L^*, π_{L+1}^*						

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:

The n_H bh-lyp orbital corresponds to the n_{H-1} hf orbital;

The π_{H-1} bh-lyp orbital corresponds to the π_H hf orbital;

The π_{L+6}^* bh-lyp orbital corresponds to the π_{L+7}^* hf orbital.

S4.9. *Dithiin*Table S38. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of **dithiin**. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
1^1B	$\pi \rightarrow \pi^*$	2.60 (0.001)	2.58 (0.001)	2.38 (0.001)	2.33 (0.001)	2.74^a
2^1A	$\pi \rightarrow \pi^*$	4.36 (0.035)	4.36 (0.038)	4.17 (0.015)	4.01 (0.010)	4.44^a
2^1B	$\pi \rightarrow \pi^*/\sigma^*$	4.54 (0.018)	4.52 (0.019)	4.26 (0.014) ¹	4.14 (0.009) ¹	5.00^a
3^1B	$\pi \rightarrow \pi^*/\sigma^*$	4.73 (0.005)	4.69 (0.006)	4.20 (0.006) ²	3.97 (0.005) ²	
3^1A	$\pi^2 \rightarrow \pi^{*2}$	4.80 (0)	4.69 (0)	4.39 (0)	4.23 (0)	
1^3B	$\pi \rightarrow \pi^*$	2.00	2.06	1.86	1.84	
2^3B	$\pi \rightarrow \pi^*/\sigma^*$	3.31	3.40	2.88	2.85	
1^3A	$\pi \rightarrow \pi^*$	3.75	3.82	3.74	3.68	
3^3B	$\pi \rightarrow \pi^*/\sigma^*$	4.36	4.36	3.91	3.81	
2^3A	$\pi \rightarrow \pi^*$	4.77	4.88	4.37	4.24	

MR-MP2(HF): $1^3\text{B}, 2^2\text{B}$ MR-MP2(BH-LYP): $1^3\text{B}, 2^2\text{B}$ ^a UV-vis absorption maximum in CH_2Cl_2 [19]

Table S39. Calculated percentage of electron configurations in the excited states wave functions of **dithiin** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
		Excitation			Excitation			Excitation	
	%	from	to	%	from	to	%	from	to
1^1B	89	π_H	π_L^*	62	π_H	π_L^*	64	π_H	π_L^*
	3	π_H	σ_{L+1}^*	2	π_H	σ_{L+1}^*	2	π_H	σ_{L+1}^*
	2	π_{H-2}	π_L^*	2	π_{H-2}	π_L^*			
2^1A	83	π_{H-1}	π_L^*	54	π_{H-1}	π_L^*	55	π_{H-1}	π_L^*
	4	π_{H-1}	σ_{L+1}^*	4	π_{H-1}	σ_{L+1}^*	3	π_{H-1}	σ_{L+1}^*
				2	π_H	π_{L+4}^*			
2^1B	44	π_H	σ_{L+1}^*	28	π_{H-2}	π_L^*	30	π_{H-2}	π_L^*
	36	π_{H-2}	π_L^*	27	π_H	σ_{L+1}^*	29	π_H	σ_{L+1}^*
	7	π_{H-2}	σ_{L+1}^*	6	π_{H-2}	σ_{L+1}^*	4	π_{H-2}	σ_{L+1}^*
	5	π_H	π_L^*	5	π_H	π_L^*	2	π_H	π_L^*
3^1B	48	π_{H-2}	π_L^*	31	π_H	σ_{L+1}^*	31	π_H	σ_{L+1}^*
	40	π_H	σ_{L+1}^*	31	π_{H-2}	π_L^*	29	π_{H-2}	π_L^*
3^1A	81	π_H, π_H	π_L^*, π_L^*	49	π_H, π_H	π_L^*, π_L^*	49	π_H, π_H	π_L^*, π_L^*
	3	π_{H-2}, π_H	π_L^*, σ_{L+1}^*	3	π_{H-2}, π_H	π_L^*, σ_{L+1}^*	3	π_{H-2}, π_H	π_L^*, σ_{L+1}^*
	2	π_{H-1}, π_{H-1}	π_L^*, π_L^*	3	n_{H-3}	π_L^*	3	π_{H-2}, π_H	π_L^*, π_L^*
				2	π_H	σ_{L+2}^*	2	n_{H-3}	π_L^*
				2	π_{H-1}, π_{H-1}	π_L^*, π_L^*			
1^3B	92	π_H	π_L^*	64	π_H	π_L^*	61	π_H	π_L^*
	2	π_{H-2}	σ_{L+1}^*	2	π_{H-2}	σ_{L+1}^*	3	π_{H-2}	π_L^*
							3	π_{H-2}	σ_{L+1}^*
2^3B	52	π_{H-2}	π_L^*	33	π_{H-2}	π_L^*	32	π_{H-2}	π_L^*
	40	π_H	σ_{L+1}^*	30	π_H	σ_{L+1}^*	31	π_H	σ_{L+1}^*
							3	π_H	π_L^*
1^3A	84	π_{H-1}	π_L^*	43	π_{H-1}	π_L^*	42	π_{H-1}	π_L^*
	4	π_H	π_{L+4}^*	12	π_H	π_{L+4}^*	10	π_H	π_{L+4}^*
				4	n_{H-3}	π_L^*	5	n_{H-3}	π_L^*
				3	π_{H-2}	π_{L+4}^*	4	π_{H-2}	π_{L+4}^*
3^3B	49	π_H	σ_{L+1}^*	29	π_{H-2}	π_L^*	28	π_{H-2}	π_L^*
	39	π_{H-2}	π_L^*	28	π_H	σ_{L+1}^*	28	π_H	σ_{L+1}^*
				4	n_{H-4}	π_L^*	5	n_{H-4}	π_L^*
				2	n_{H-4}	σ_{L+1}^*	2	n_{H-4}	σ_{L+1}^*
2^3A	23	π_H	π_{L+4}^*	16	π_{H-1}	σ_{L+1}^*	17	π_{H-1}	σ_{L+1}^*
	21	π_H	σ_{L+2}^*	12	π_{H-1}	π_L^*	16	π_{H-1}	π_L^*
	18	π_{H-1}	σ_{L+1}^*	10	π_H	π_{L+4}^*	9	π_H	π_{L+4}^*
	17	n_{H-3}	π_L^*	8	n_{H-3}	π_L^*	9	n_{H-3}	π_L^*
	6	π_{H-6}	π_L^*	7	π_H	σ_{L+2}^*	6	π_{H-6}	π_L^*
	3	π_{H-2}	π_{L+4}^*	6	π_{H-6}	π_L^*	5	π_H	σ_{L+2}^*
				2	π_{H-2}	σ_{L+2}^*	3	π_{H-2}	π_{L+4}^*

The orbitals presented in the table are labeled according to the orbital obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different:

- The π_{H-2} bh-lyp orbital corresponds to the π_{H-1} hf orbital;
- The π_{H-1} bh-lyp orbital corresponds to the π_{H-2} hf orbital;
- The σ_{L+2}^* bh-lyp orbital corresponds to the σ_{L+3}^* hf orbital.
- The Ry_{L+3} bh-lyp orbital corresponds to the Ry_{L+2} hf orbital.
- The π_{L+4}^* bh-lyp orbital corresponds to the π_{L+5}^* hf orbital.

S4.10. *Bithiophene*Table S40. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of *s-trans* **bithiophene**. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
1 ¹ B	$\pi \rightarrow \pi^*$	4.17 (0.446)	4.15 (0.472)	4.02 (0.437)	3.93 (0.401)	3.86 ^a , 4.09 (4.11) ^b
2 ¹ A	$\pi \rightarrow \pi^*$	4.81 (0.005)	4.87 (0.006)	4.66 (0.001)	4.39 (0) ¹	
2 ¹ B	$\pi \rightarrow \pi^*$	4.95 (0.112)	5.00 (0.129)	4.58 (0.092)	4.18 (0.066)	
3 ¹ A	$\pi \rightarrow \pi^*$	5.02 (0.003)	5.11 (0.004)	4.69 (0.003)	4.28 (0.002) ²	
4 ¹ A	$\pi \rightarrow \sigma^*$	5.34 (0.001)	5.39 (0.002)	5.27 (0.001) ¹	4.81 (0) ³	
3 ¹ B	$\pi \rightarrow \sigma^*$	5.42 (0.023)	5.46 (0.029)	5.44 (0.030)	4.92 (0.028)	
1 ³ B	$\pi \rightarrow \pi^*$	2.78	2.81	2.62	2.44	2.32 ^a
1 ³ A	$\pi \rightarrow \pi^*$	3.72	3.79	3.50	3.25	
2 ³ A	$\pi \rightarrow \pi^*$	4.17	4.22	4.02	3.72	
2 ³ B	$\pi \rightarrow \pi^*$	4.21	4.26	3.98	3.71	
3 ³ B	$\pi \rightarrow \sigma^*$	5.09	5.14	5.03	4.55	
3 ³ A	$\pi \rightarrow \sigma^*$	5.09	5.14	5.35	4.76	
4 ³ B	$\pi \rightarrow \pi^*$	5.43	5.49	5.46	4.76	
4 ³ A	$\pi \rightarrow \pi^*$	5.45	5.39	5.38	4.92	

MRMP2(HF): 1⁵1AMRMP2(BH-LYP): 1³1A, 2²1A, 3⁵1A^a PD-PES in the gas phase [20]^b Absorption maximum in dioxane. [21]^b Value in parentheses is for the spectra in methylcyclohexane [21]

Table S41.: Calculated percentage of electron configurations in the excited states wave functions of *s-trans* **bithiophene** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
		Excitation			Excitation			Excitation	
	%	from	to	%	from	to	%	from	to
1 ¹ B	89	π_H	π_L^*	58	π_H	π_L^*	56	π_H	π_L^*
2 ¹ A	54	π_{H-1}	π_L^*	21	π_H	π_{L+1}^*	21	π_H	π_{L+1}^*
	16	π_H	π_{L+1}^*	21	π_{H-1}	π_L^*	12	π_{H-1}	π_L^*
	4	π_{H-2}	π_{L+1}^*	8	π_H, π_H	π_L^*, π_L^*	12	π_H, π_H	π_L^*, π_L^*
	3	π_{H-3}	π_L^*	3	π_{H-3}	π_L^*	7	π_{H-3}	π_L^*
	3	π_H, π_H	π_L^*, π_L^*	2	π_{H-3}, π_H	π_L^*, π_{L+1}^*	3	π_{H-3}, π_H	π_L^*, π_{L+1}^*
	2	π_{H-2}, π_H	π_L^*, π_L^*						
	2	π_H	σ_{L+2}^*						
2 ¹ B	65	π_{H-2}	π_L^*	40	π_{H-2}	π_L^*	35	π_{H-2}	π_L^*
	5	π_H	π_{L+6}^*	5	π_H	π_{L+6}^*	8	π_H	σ_{L+3}^*
	5	π_H	σ_{L+3}^*	4	π_H	σ_{L+3}^*	5	π_H	π_{L+6}^*
	3	π_H, π_{H-1}	π_L^*, π_L^*	3	π_H, π_{H-1}	π_L^*, π_L^*	3	π_H, π_{H-1}	π_L^*, π_L^*
	3	π_{H-1}	π_{L+1}^*	2	π_H	Ry_{L+4}	2	π_H	Ry_{L+4}
	2	π_H	Ry_{L+4}						
1 ³ B	87	π_H	π_L^*	56	π_H	π_L^*	54	π_H	π_L^*
	5	π_{H-3}	π_{L+1}^*	5	π_{H-3}	π_{L+1}^*	6	π_{H-3}	π_{L+1}^*
1 ³ A	51	π_H	π_{L+1}^*	33	π_H	π_{L+1}^*	32	π_H	π_{L+1}^*
	37	π_{H-3}	π_L^*	24	π_{H-3}	π_L^*	25	π_{H-3}	π_L^*
2 ³ A	73	π_{H-1}	π_L^*	42	π_{H-1}	π_L^*	42	π_{H-1}	π_L^*
	11	π_{H-2}	π_{L+1}^*	10	π_{H-2}	π_{L+1}^*	10	π_{H-2}	π_{L+1}^*
	3	π_{H-3}	π_L^*	4	π_{H-3}	π_L^*	2	π_H	π_{L+7}^*
							2	π_{H-3}	π_L^*
2 ³ B	67	π_{H-2}	π_L^*	39	π_{H-2}	π_L^*	38	π_{H-2}	π_L^*
	14	π_{H-1}	π_{L+1}^*	12	π_{H-1}	π_{L+1}^*	11	π_{H-1}	π_{L+1}^*
	5	π_H	π_{L+6}^*	5	π_H	π_{L+6}^*	4	π_H	π_{L+6}^*
	2	π_H	σ_{L+3}^*	2	π_{H-3}	π_{L+1}^*	2	π_{H-3}	π_{L+1}^*
	2	π_H	Ry_{L+4}				2	π_H	σ_{L+3}^*
	2	π_{H-3}	π_{L+1}^*				2	π_H	Ry_{L+4}
3 ³ B	63	π_H	σ_{L+3}^*	15	π_H	σ_{L+3}^*	27	π_H	σ_{L+3}^*
	9	π_{H-3}	π_{L+1}^*	12	π_H	π_{L+6}^*	9	π_{H-3}	π_{L+1}^*
	7	π_{H-2}	π_L^*	11	π_{H-3}	π_{L+1}^*	8	π_{H-2}	π_L^*
	3	π_H	π_{L+6}^*	10	π_{H-2}	π_L^*	6	π_H	π_{L+6}^*
	2	π_{H-6}	π_L^*	7	π_H	Ry_{L+4}	3	π_{H-6}	π_L^*
				3	π_{H-6}	π_L^*	2	π_H	Ry_{L+4}
							2	π_H	π_L^*
3 ³ A	76	π_H	σ_{L+2}^*	22	π_H	σ_{L+2}^*	41	π_H	σ_{L+2}^*
	3	π_{H-3}	σ_{L+3}^*	12	π_H	Ry_{L+5}	4	π_{H-1}	π_L^*
	2	π_H	Ry_{L+5}	6	π_H	π_{L+7}^*	4	π_{H-3}	π_{L+6}^*
				5	π_{H-1}	π_L^*	3	π_H	Ry_{L+5}
				4	π_{H-3}	π_{L+6}^*	2	π_H	π_{L+7}^*
				3	π_H	Ry_{L+10}	2	π_{H-3}	Ry_{L+4}
				2	π_H	π_{L+1}^*			
				2	π_{H-3}	π_L^*			

Continued on next page

Table S41 – continued from previous page

DFT/MRCI				MRMP2			MRMP2		
(BH-LYP)				(HF)			(BH-LYP)		
Excitation				Excitation			Excitation		
State	%	from	to	%	from	to	%	from	to
				2	π_{H-3}	Ry_{L+11}			
4 ³ B	33	π_H	π_{L+6}^*	20	π_H	σ_{L+3}^*	20	π_H	σ_{L+3}^*
	12	π_H	σ_{L+3}^*	11	π_H	Ry_{L+11}	15	π_H	π_{L+6}^*
	12	π_H	Ry_{L+4}	7	π_H	π_{L+6}^*	8	π_{H-3}	σ_{L+2}^*
	9	π_{H-3}	σ_{L+2}^*	4	π_{H-3}	σ_{L+2}^*	5	π_H	Ry_{L+4}
	9	π_{H-3}	π_{L+1}^*	4	π_{H-1}	Ry_{L+2}	3	π_{H-1}	Ry_{L+2}
	6	π_{H-2}	π_L^*	3	π_{H-3}	π_{L+1}^*	3	π_{H-3}	π_{L+1}^*
	4	π_{H-6}	π_L^*	3	π_H	Ry_{L+4}			
4 ³ A	34	π_{H-3}	π_L^*	17	π_H	σ_{L+2}^*	11	π_{H-3}	π_L^*
	27	π_H	π_{L+1}^*	12	π_{H-3}	π_L^*	11	π_H	π_{L+1}^*
	7	π_{H-1}	π_L^*	11	π_H	π_{L+1}^*	10	π_H	σ_{L+2}^*
	6	π_H	π_{L+7}^*	5	π_{H-3}	σ_{L+3}^*	7	π_H	π_{L+7}^*
	4	π_{H-3}	π_{L+6}^*	5	π_H	Ry_{L+10}	7	π_{H-3}	σ_{L+3}^*
	3	π_H	Ry_{L+5}				3	π_{H-1}	π_L^*
	3	π_{H-3}	σ_{L+3}^*				2	π_H	Ry_{L+5}
	2	π_H	Ry_{L+10}				2	π_H	Ry_{L+9}
	2	π_H	Ry_{L+9}				2	π_{H-3}	π_{L+6}^*
							2	π_H	Ry_{L+10}

The orbitals presented in the table are labeled according to the order obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different:

The π_{L+7}^* bh-lyp orbital corresponds to the π_{L+8}^* hf orbital;

The Ry_{L+10} bh-lyp orbital corresponds to the Ry_{L+11} hf orbital;

The Ry_{L+11} bh-lyp orbital corresponds to the Ry_{L+10} hf orbital.

S4.11. *Nitromethane*Table S42. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of **nitromethane** using the valence basis. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
$1^1A''$	$n \rightarrow \pi^*$	3.92 (0)	4.00 (0)	3.83 (0)	3.77 (0)	4.25^a
$2^1A''$	$n \rightarrow \pi^*$	4.34 (0)	4.36 (0)	4.04 (0)	4.07 (0)	4.50^b , 4.45 ^c , 4.51 ^d , 4.59 ^e
$2^1A'$	$\pi \rightarrow \pi^*$	6.39 (0.260)	6.44 (0.305)	6.46 (0.209)	6.47 (0.198)	6.25^b , 6.23 ^{a,c} , 6.29 ^d , 6.26 ^e
$3^1A'$	$\pi \rightarrow \pi^*$	8.86 (0.093)	9.02 (0.045) [†]	8.60 (0.196) ¹	8.59 (0.260) ¹	
$4^1A'$	$\pi \rightarrow Ryd$	8.92 (0.007)	8.88 (0.002)	8.58 (0.019) ²	8.54 (0.003) ²	
$1^3A'$	$\pi \rightarrow \pi^*$	3.43	3.31	3.54	3.55	
$1^3A''$	$n \rightarrow \pi^*$	3.71	3.80	3.55	3.60	
$2^3A''$	$n \rightarrow \pi^*$	4.10	4.13	3.85	3.92	
$2^3A'$	$n, n \rightarrow \pi^{*2}$	7.51	6.25	8.66 ³	8.85 ³	
$3^3A'$	$\pi \rightarrow \pi^*$	7.98	8.13	8.27 ⁴	8.26 ⁴	
$4^3A'$	$\pi \rightarrow Ryd$	8.81	8.75	8.44 ⁵	8.40 ⁵	

[†] $5^1A'$ MRMP2(HF): $1^4A'$, $2^3A'$, $3^4A'$, $4^2A'$, $5^3A'$ MRMP2(BHLYP): $1^4A'$, $2^3A'$, $3^6A'$, $4^2A'$, $5^3A'$ ^a Electron energy-loss maximum in gas [22]^b Absorption maximum in gas [22]^c Electron energy-loss maximum in gas[23]^d Absorption maximum in gas [24]^e Absorption maximum in gas [25]

Table S43.: Calculated percentage of electron configurations in the excited states wave functions of **nitromethane** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
		Excitation			Excitation			Excitation	
	%	from	to	%	from	to	%	from	to
$1^1A''$	90	n_{H-1}	π_L^*	62	n_{H-1}	π_L^*	70	n_{H-1}	π_L^*
	7	n_{H-2}, π_H	π_L^*, π_L^*	7	n_{H-2}	π_L^*	6	n_{H-2}, π_H	π_L^*, π_L^*
				5	n_{H-2}, π_H	π_L^*, π_L^*			
				2	n_{H-1}	Ry_{L+4}			
$2^1A''$	89	n_{H-2}	π_L^*	62	n_{H-2}	π_L^*	71	n_{H-2}	π_L^*
	8	n_{H-1}, π_H	π_L^*, π_L^*	8	n_{H-1}	π_L^*	6	n_{H-1}, π_H	π_L^*, π_L^*
				6	n_{H-1}, π_H	π_L^*, π_L^*			
				2	n_{H-2}	Ry_{L+4}			
$2^1A'$	83	π_H	π_L^*	65	π_H	π_L^*	63	π_H	π_L^*
	6	π_{H-7}, π_H	π_L^*, π_L^*	6	π_{H-7}, π_H	π_L^*, π_L^*	9	π_{H-7}, π_H	π_L^*, π_L^*
	4	π_{H-3}, π_H	π_L^*, π_L^*	3	π_{H-3}, π_H	π_L^*, π_L^*	3	π_{H-3}, π_H	π_L^*, π_L^*
$1^3A'$	98	π_H	π_L^*	78	π_H	π_L^*	80	π_H	π_L^*
				2	π_H	Ry_{L+4}			
$1^3A''$	93	n_{H-1}	π_L^*	64	n_{H-1}	π_L^*	71	n_{H-1}	π_L^*
	3	n_{H-2}, π_H	π_L^*, π_L^*	6	n_{H-2}	π_L^*	4	n_{H-2}, π_H	π_L^*, π_L^*
				4	n_{H-2}, π_H	π_L^*, π_L^*			
				2	n_{H-1}	Ry_{L+4}			
$2^3A''$	94	n_{H-2}	π_L^*	65	n_{H-2}	π_L^*	72	n_{H-2}	π_L^*
	4	n_{H-1}, π_H	π_L^*, π_L^*	7	n_{H-1}	π_L^*	5	n_{H-1}, π_H	π_L^*, π_L^*
				5	n_{H-1}, π_H	π_L^*, π_L^*			
				2	n_{H-2}	Ry_{L+4}			

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:

The π_{H-7} bh-lyp orbital corresponds to the π_{H-6} hf orbital;

The n_{H-1} bh-lyp orbital corresponds to the n_{H-2} hf orbital;

The n_{H-2} bh-lyp orbital corresponds to the n_{H-1} hf orbital.

Table S44. Selected matrix elements (cm^{-1}) for **nitromethane** calculated with DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) methods using the valence basis.

	SOMEs(cm^{-1})			
	DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)
$\langle 1^3 A' \hat{\mathcal{H}}_{\text{SO } z} 1^1 A' \rangle$	0.3	0.3	0.2	0.0
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } x} 1^1 A' \rangle$	33.9	32.8	31.8	36.6
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } x} 2^1 A' \rangle$	17.0	16.0	17.2	17.4
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } y} 1^1 A' \rangle$	16.5	16.7	22.8	18.0
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } y} 2^1 A' \rangle$	30.1	28.6	30.7	30.6
$\langle 1^3 A' \hat{\mathcal{H}}_{\text{SO } x} 1^1 A'' \rangle$	23.8	23.3	22.3	23.7
$\langle 1^3 A' \hat{\mathcal{H}}_{\text{SO } x} 2^1 A'' \rangle$	9.5	9.4	10.6	7.9
$\langle 1^3 A' \hat{\mathcal{H}}_{\text{SO } y} 1^1 A'' \rangle$	41.1	40.5	42.1	41.5
$\langle 1^3 A' \hat{\mathcal{H}}_{\text{SO } y} 2^1 A'' \rangle$	6.7	6.3	1.2	5.3
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } z} 2^1 A'' \rangle$	32.8	32.3	35.1	35.7
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } x} 1^3 A' \rangle$	22.6	23.1	22.3	23.5
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } y} 1^3 A' \rangle$	39.0	40.0	41.2	40.7
$\langle 2^3 A'' \hat{\mathcal{H}}_{\text{SO } z} 1^3 A'' \rangle$	33.9	32.5	35.5	35.9

Table S45. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF), MR-MP2(BH-LYP), CASPT2 (8,7) and CASPT2 (8,6) vertical excitation energies of **nitromethane** using the augmented basis. The CASPT2 (8,7) active space consists of following occupied/unoccupied orbitals: $2/2\ a'$ and $2/1\ a''$. The (8,6) active space has one a' orbital less. The oscillator strengths are given in the parentheses.

State	Dominant character	DFT/MRCI	DFT/MRCI-R	Energies (eV)				Experiment
				MRMP2 (HF)	MRMP2 (BH-LYP)	CASPT2 (8,7)	CASPT2 (8,6)	
$1^1A''$	$n \rightarrow \pi^*$	3.83 (0)	3.92 (0)	3.64 (0)	3.71 (0)	3.92 (0)	3.88 (0)	4.25^a
$2^1A''$	$n \rightarrow \pi^*$	4.26 (0)	4.28 (0)	3.97 (0)	4.03 (0)	4.32 (0)	4.33 (0)	4.50^b , 4.45 ^c , 4.51 ^d , 4.59 ^e
$2^1A'$	$\pi \rightarrow \pi^*$	6.30 (0.257)	6.34 (0.297)	6.18 (0.204)	6.31 (0.200)	6.38 (0.260)	5.63 (0.384)	6.25^b , 6.23 ^{a,c} , 6.29 ^d , 6.26 ^e
$3^1A'$	$n \rightarrow 3s$	7.74 (0.008)	7.66 (0.007)	7.55 (0.004)	7.49 (0.010)	7.07 (0.033)	7.42 (0.003)	
$4^1A'$	$n \rightarrow 3s$	8.00 (0.041)	7.87 (0.042)	7.62 (0.022)	7.72 (0.033)	7.55 (0.078)	7.80 (0)	
$1^3A'$	$\pi \rightarrow \pi^*$	3.36	3.30	3.54	3.57	3.65	3.70	
$1^3A''$	$n \rightarrow \pi^*$	3.61	3.72	3.42	3.52	3.66	3.66	
$2^3A''$	$n \rightarrow \pi^*$	4.01	4.06	3.80	3.93	4.15	4.16	
$2^3A'$	$n, n \rightarrow \pi^{*2}$	7.31	6.12	8.70 ¹	8.79 ¹	8.97	9.01	
$3^3A'$	$n \rightarrow 3s$	7.65	7.56	7.50 ²	7.46 ²	7.43	7.48	
$4^3A'$	$n \rightarrow 3s$	7.91	7.79	7.51 ³	7.57 ³	7.73	7.73	
MRMP2(HF): ¹ $5^3A'$, $2^3A'$, $3^3A'$								
MRMP2(BH-LYP): ¹ $8^3A'$, $2^3A'$, $3^3A'$								
^a Electron energy-loss maximum in gas [22]								
^b Absorption maximum in gas [22]								
^c Electron energy-loss maximum in gas [23]								
^d Absorption maximum in gas [24]								
^e Absorption maximum in gas [25]								

Table S46.: Calculated percentage of electron configurations in the excited states wave functions of **nitromethane** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	Excitation			Excitation			Excitation		
	%	from	to	%	from	to	%	from	to
$1^1A''$	86	n_{H-1}	π_L^*	52	n_{H-1}	π_L^*	68	n_{H-1}	π_L^*
	6	n_{H-2}, π_H	π_L^*, π_L^*	10	n_{H-1}	π^*/pz	5	n_{H-2}, π_H	π_L^*, π_L^*
				6	n_{H-1}	π^*/pz'			
$2^1A''$	86	n_{H-2}	π_L^*	52	n_{H-2}	π_L^*	68	n_{H-2}	π_L^*
	7	n_{H-1}, π_H	π_L^*, π_L^*	10	n_{H-2}	π^*/pz	6	n_{H-1}, π_H	π_L^*, π_L^*
				6	n_{H-2}	π^*/pz'			
$2^1A'$	82	π_H	π_L^*	39	π_H	π_L^*	63	π_H	π_L^*
	6	π_{H-7}, π_H	π_L^*, π_L^*	16	π_H	π^*/pz	8	π_{H-7}, π_H	π_L^*, π_L^*
				11	π_H	π^*/pz'			
$1^3A'$	94	π_H	π_L^*	62	π_H	π_L^*	77	π_H	π_L^*
				11	π_H	π^*/pz			
				6	π_H	π^*/pz'			
$1^3A''$	89	n_{H-1}	π_L^*	54	n_{H-1}	π_L^*	68	n_{H-1}	π_L^*
				9	n_{H-1}	π^*/pz			
				6	n_{H-1}	π^*/pz'			
$2^3A''$	90	n_{H-2}	π_L^*	54	n_{H-2}	π_L^*	69	n_{H-2}	π_L^*
				10	n_{H-2}	π^*/pz	5	n_{H-1}, π_H	π_L^*, π_L^*
				6	n_{H-2}	π^*/pz'			

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:

The π_L^* bh-lyp orbital corresponds to the π_{L+9}^* hf orbital;

The n_{H-1} bh-lyp orbital corresponds to the n_{H-2} hf orbital;

The n_{H-2} bh-lyp orbital corresponds to the n_{H-1} hf orbital.

Table S47.: Calculated percentage of electron configurations in the discussed wave functions of **nitromethane** obtained at the DFT/MRCI-R, CASPT2 (8,7) and CASPT2 (8,6) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

DFT/MRCI-R				CASPT2 (8,7)			CASPT2 (8,6)		
State	%	Excitation		%	Excitation		%	Excitation	
		from	to		from	to		from	to
$1^1A''$	88	n_{H-1}	π_L^*	86	n_{H-1}	π_L^*	84	n_{H-1}	π_L^*
	5	n_{H-2}, π_H	π_L^*, π_L^*	11	n_{H-2}, π_H	π_L^*, π_L^*	16	n_{H-2}, π_H	π_L^*, π_L^*
$2^1A''$	87	n_{H-2}	π_L^*	82	n_{H-2}	π_L^*	81	n_{H-2}	π_L^*
	6	n_{H-1}, π_H	π_L^*, π_L^*	16	n_{H-1}, π_H	π_L^*, π_L^*	19	n_{H-1}, π_H	π_L^*, π_L^*
$2^1A'$	85	π_H	π_L^*	57	π_H	π_L^*	81	π_H	π_L^*
	5	π_{H-7}, π_H	π_L^*, π_L^*	12	n_{H-1}	$3s$	15	π_{H-7}, π_H	π_L^*, π_L^*
				10	n_{H-2}	$3s$			
				8	π_{H-7}, π_H	π_L^*, π_L^*			
$1^3A'$	95	π_H	π_L^*	97	π_H	π_L^*	98	π_H	π_L^*
$1^3A''$	89	n_{H-1}	π_L^*	88	n_{H-1}	π_L^*	86	n_{H-1}	π_L^*
				9	n_{H-2}, π_H	π_L^*, π_L^*	14	n_{H-2}, π_H	π_L^*, π_L^*
$2^3A''$	89	n_{H-2}	π_L^*	84	n_{H-2}	π_L^*	83	n_{H-2}	π_L^*
	5	n_{H-1}, π_H	π_L^*, π_L^*	13	n_{H-1}, π_H	π_L^*, π_L^*	17	n_{H-1}, π_H	π_L^*, π_L^*

S4.12. NitrobenzeneTable S48. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of **nitrobenzene**. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
1^1A_2	$n \rightarrow \pi^*$	3.29 (0)	3.46 (0)	3.25 (0)	3.47 (0)	3.65^a
1^1B_2	$n \rightarrow \pi^*$	3.88 (0)	3.91 (0)	3.82 (0)	3.76 (0)	
1^1B_1	$\pi \rightarrow \pi^*$	4.29 (0.004)	4.40 (0.021)	4.28 (0.006)	4.18 (0.004)	
2^1B_1	$\pi, \pi \rightarrow \pi^*, \pi^*$	4.63 (0.024)		7.19 (0.170) ¹	7.00 (0.198) ¹	5.17^b
2^1A_1	$\pi \rightarrow \pi^*$	4.77 (0.249)	4.81 (0.311)	5.33 (0.246)	5.08 (0.243)	
1^3B_1	$\pi \rightarrow \pi^*$	2.84	2.93	3.35	3.35	
1^3A_2	$n \rightarrow \pi^*$	3.11	3.26	3.00	3.09	
1^3A_1	$\pi \rightarrow \pi^*$	3.66	3.65	3.62	3.51	
1^3B_2	$n \rightarrow \pi^*$	3.67	3.72	3.63	3.62	
2^3B_1	$\pi \rightarrow \pi^*$	4.01	4.01	4.34	4.18	
$\vdots$						
4^3B_1	$\pi, \pi \rightarrow \pi^*, \pi^*$	5.88				

MR-MP2(HF): $^1 5^1B_1$ MR-MP2(HF): $^1 5^1B_1$ ^a Absorption maximum in n-hexane [26]^b Absorption maximum in gas phase [26]

Table S49. Calculated percentage of electron configurations in the excited states wave functions of **nitrobenzene** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	%	Excitation		%	Excitation		%	Excitation	
		from	to		from	to		from	to
1^1A_2	77	n_{H-3}	π_L^*	45	n_{H-3}	π_L^*	50	n_{H-3}	π_L^*
	12	n_{H-3}	π_{L+2}^*	12	n_{H-3}	π_{L+2}^*	7	n_{H-3}	π_{L+2}^*
	3	n_{H-4}, π_{H-2}	π_L^*, π_L^*	3	n_{H-4}, π_{H-2}	π_L^*, π_L^*	3	n_{H-4}, π_{H-2}	π_L^*, π_L^*
				2	n_{H-4}, π_{H-2}	π_L^*, π_{L+2}^*			
1^1B_2	76	n_{H-4}	π_L^*	45	n_{H-4}	π_L^*	50	n_{H-4}	π_L^*
	11	n_{H-4}	π_{L+2}^*	12	n_{H-4}	π_{L+2}^*	6	n_{H-4}	π_{L+2}^*
	4	n_{H-3}, π_{H-2}	π_L^*, π_L^*	3	n_{H-3}, π_{H-2}	π_L^*, π_L^*	4	n_{H-3}, π_{H-2}	π_L^*, π_L^*
				2	n_{H-3}, π_{H-2}	π_L^*, π_{L+2}^*	2	n_{H-3}, π_{H-2}	π_L^*, π_{L+2}^*
1^1B_1	46	π_H	π_L^*	35	π_H	π_L^*	26	π_H	π_L^*
	26	π_{H-2}, π_H	π_L^*, π_{L+1}^*	21	π_{H-1}	π_{L+1}^*	23	π_{H-1}	π_{L+1}^*
	5	π_{H-1}	π_{L+1}^*	4	π_H	π_{L+2}^*	8	π_H	π_{L+2}^*
	5	π_{H-2}, π_{H-1}	π_L^*, π_L^*						
	4	π_{H-2}, π_H	π_{L+1}^*, π_{L+2}^*						
	3	π_{H-2}	π_L^*						
2^1B_1	33	π_{H-2}, π_H	π_L^*, π_{L+1}^*	24	π_{H-2}, π_H	π_L^*, π_{L+1}^*	28	π_{H-2}, π_H	π_L^*, π_{L+1}^*
	25	π_H	π_L^*	10	π_{H-1}, π_H	π_{L+1}^*, π_{L+2}^*	6	π_{H-1}, π_H	π_{L+1}^*, π_{L+2}^*
	12	π_{H-1}	π_{L+1}^*	8	π_{H-2}	π_{L+2}^*	5	π_{H-2}, π_{H-1}	π_L^*, π_L^*
	5	π_{H-2}	π_L^*	7	π_{H-2}, π_{H-1}	π_L^*, π_L^*	5	π_{H-1}	π_{L+1}^*
	5	π_{H-2}, π_{H-1}	π_L^*, π_L^*	3	π_{H-1}	π_{L+1}^*	4	π_{H-2}	π_{L+2}^*
2^1A_1	75	π_{H-1}	π_L^*	54	π_{H-1}	π_L^*	50	π_{H-1}	π_L^*
	5	π_{H-2}, π_{H-1}	π_L^*, π_{L+1}^*	7	π_H	π_{L+1}^*	6	π_H	π_{L+1}^*
	3	π_{H-2}, π_H	π_L^*, π_L^*						
	2	π_{H-2}	π_{L+1}^*						
	2	π_H	π_{L+1}^*						
1^3B_1	77	π_{H-2}	π_L^*	49	π_{H-2}	π_L^*	53	π_{H-2}	π_L^*
	15	π_{H-2}	π_{L+2}^*	16	π_{H-2}	π_{L+2}^*	10	π_{H-2}	π_{L+2}^*
	4	π_H	π_L^*						
1^3A_2	78	n_{H-3}	π_L^*	46	n_{H-3}	π_L^*	51	n_{H-3}	π_L^*
	13	n_{H-3}	π_{L+2}^*	13	n_{H-3}	π_{L+2}^*	7	n_{H-3}	π_{L+2}^*
	2	n_{H-4}, π_{H-2}	π_L^*, π_L^*	2	n_{H-4}, π_{H-2}	π_L^*, π_L^*	3	n_{H-4}, π_{H-2}	π_L^*, π_L^*
1^3A_1	77	π_{H-1}	π_L^*	38	π_{H-1}	π_L^*	30	π_{H-1}	π_L^*
	9	π_{H-1}	π_{L+2}^*	15	π_H	π_{L+1}^*	17	π_H	π_{L+1}^*
	8	π_H	π_{L+1}^*	8	π_{H-1}	π_{L+2}^*	13	π_{H-1}	π_{L+2}^*
1^3B_2	78	n_{H-4}	π_L^*	46	n_{H-4}	π_L^*	51	n_{H-4}	π_L^*
	12	n_{H-4}	π_{L+2}^*	13	n_{H-4}	π_{L+2}^*	7	n_{H-4}	π_{L+2}^*
	2	n_{H-3}, π_{H-2}	π_L^*, π_L^*	2	n_{H-3}, π_{H-2}	π_L^*, π_L^*	4	n_{H-3}, π_{H-2}	π_L^*, π_L^*
4^3B_1	55	π_{H-2}, π_H	π_L^*, π_{L+1}^*						
	9	π_{H-1}, π_H	π_{L+1}^*, π_{L+2}^*						
	7	π_{H-2}, π_{H-1}	π_L^*, π_L^*						
	6	π_{H-1}	π_{L+1}^*						

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:

The π_{L+2}^* bh-lyp orbital corresponds to the π_{L+3}^* hf orbital;

Table S50.: Calculated percentage of electron configurations in the excited states wave functions of **nitrobenzene** obtained at the DFT/MRCI, and DFT/MRCI-R levels of theory. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			DFT/MRCI-R		
	%	Excitation		%	Excitation	
		from	to		from	to
1^1A_2	77	n_{H-3}	π_L^*	78	n_{H-3}	π_L^*
	12	n_{H-3}	π_{L+2}^*	12	n_{H-3}	π_{L+2}^*
	3	n_{H-4}, π_{H-2}	π_L^*, π_L^*	4	n_{H-4}, π_{H-2}	π_L^*, π_L^*
1^1B_2	76	n_{H-4}	π_L^*	75	n_{H-4}	π_L^*
	11	n_{H-4}	π_{L+2}^*	10	n_{H-4}	π_{L+2}^*
	4	n_{H-3}, π_{H-2}	π_L^*, π_L^*	5	n_{H-3}, π_{H-2}	π_L^*, π_L^*
1^1B_1	46	π_H	π_L^*	73	π_H	π_L^*
	26	π_{H-2}, π_H	π_L^*, π_{L+1}^*	14	π_{H-1}	π_{L+1}^*
	5	π_{H-1}	π_{L+1}^*			
	5	π_{H-2}, π_{H-1}	π_L^*, π_L^*			
	4	π_{H-2}, π_H	π_{L+1}^*, π_{L+2}^*			
	3	π_{H-2}	π_L^*			
2^1B_1	33	π_{H-2}, π_H	π_L^*, π_{L+1}^*			
	25	π_H	π_L^*			
	12	π_{H-1}	π_{L+1}^*			
	5	π_{H-2}	π_L^*			
	5	π_{H-2}, π_{H-1}	π_L^*, π_L^*			
2^1A_1	75	π_{H-1}	π_L^*	86	π_{H-1}	π_L^*
	5	π_{H-2}, π_{H-1}	π_L^*, π_{L+1}^*	2	π_H	π_{L+1}^*
	3	π_{H-2}, π_H	π_L^*, π_L^*			
	2	π_{H-2}	π_{L+1}^*			
	2	π_H	π_{L+1}^*			
1^3B_1	77	π_{H-2}	π_L^*	79	π_{H-2}	π_L^*
	15	π_{H-2}	π_{L+2}^*	13	π_{H-2}	π_{L+2}^*
	4	π_H	π_L^*	4	π_H	π_L^*
1^3A_2	78	n_{H-3}	π_L^*	78	n_{H-3}	π_L^*
	13	n_{H-3}	π_{L+2}^*	12	n_{H-3}	π_{L+2}^*
	2	n_{H-4}, π_{H-2}	π_L^*, π_L^*	3	n_{H-4}, π_{H-2}	π_L^*, π_L^*
1^3A_1	77	π_{H-1}	π_L^*	77	π_{H-1}	π_L^*
	9	π_{H-1}	π_{L+2}^*	9	π_{H-1}	π_{L+2}^*
	8	π_H	π_{L+1}^*	7	π_H	π_{L+1}^*
1^3B_2	78	n_{H-4}	π_L^*	77	n_{H-4}	π_L^*
	12	n_{H-4}	π_{L+2}^*	11	n_{H-4}	π_{L+2}^*
	2	n_{H-3}, π_{H-2}	π_L^*, π_L^*	4	n_{H-3}, π_{H-2}	π_L^*, π_L^*
4^3B_1	55	π_{H-2}, π_H	π_L^*, π_{L+1}^*			
	9	π_{H-1}, π_H	π_{L+1}^*, π_{L+2}^*			
	7	π_{H-2}, π_{H-1}	π_L^*, π_L^*			
	6	π_{H-1}	π_{L+1}^*			

S4.13. DithiosuccinimideTable S51. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of **dithiosuccinimide**. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
1^1B_1	$n \rightarrow \pi^*$	2.66 (0)	2.73 (0)	2.58 (0)	2.45 (0)	2.77^a , 2.82 ^b
1^1A_2	$n \rightarrow \pi^*$	2.85 (0)	2.93 (0)	2.80 (0)	2.66 (0)	3.04^a , 3.08 ^b
1^1B_2	$\pi \rightarrow \pi^*$	4.13 (0.722)	4.09 (0.7222)	3.85 (0.585)	3.75 (0.544)	3.96^a , 3.87 ^b
2^1A_2	$n \rightarrow \pi^*$	4.64 (0)	4.64 (0)	4.37 (0)	4.00 (0)	
2^1A_1	$n, n \rightarrow \pi^*, \pi^*$	4.71 (0)	3.40 (0)			
2^1B_1	$n \rightarrow \pi^*$	4.83 (0)	4.80 (0)	4.55 (0)	4.20 (0)	
$\vdots$						
5^1A_1	$n^2 \rightarrow \pi^{*2}$	6.07 (0)	5.08 (0) ¹	5.51 (0) ¹	5.26(0) ¹	
1^3B_1	$n \rightarrow \pi^*$	2.44	2.57	2.42	2.42	2.63^a
1^3A_2	$n \rightarrow \pi^*$	2.64	2.77	2.67	2.59	
1^3B_2	$\pi \rightarrow \pi^*$	2.77	2.84	2.67	2.55	
1^3A_1	$\pi \rightarrow \pi^*$	3.43	3.51	3.42	3.28	
2^3B_2	$n, n \rightarrow \pi^{*2}$	4.60	3.87	5.70 ²	5.29 ²	
2^3A_1	$n, n \rightarrow \pi^*, \pi^*$	4.68	3.36 ²	6.67 ³	6.55 ³	
2^3A_2	$n \rightarrow \pi^*$	4.70	4.60	4.38	4.03	
2^3B_1	$n \rightarrow \pi^*$	4.87	4.73	4.50	4.14	

DFT/MRCI-R: ¹ 3^1A_1 , ² 1^3A_1 MRMP2(HF): ¹ 4^1A_1 , ² 3^3B_2 , ³ 4^3A_1 MRMP2(BH-LYP): ¹ 4^1A_1 , ² 3^3B_2 , ³ 5^3A_1 ^a Absorption maximum in cyclohexane [27]^b Absorption maximum in methanol [27]

Table S52.: Calculated percentage of electron configurations in the excited states wave functions of **dithiosuccinimide** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	%	Excitation		%	Excitation		%	Excitation	
		from	to		from	to		from	to
1^1B_1	81	n_H	π_L^*	53	n_H	π_L^*	50	n_H	π_L^*
	11	n_{H-1}	π_{L+1}^*	10	n_{H-1}	π_{L+1}^*	12	n_{H-1}	π_{L+1}^*
				2	n_{H-1}, π_{H-2}	π_L^*, π_L^*	2	n_{H-1}, π_{H-2}	π_L^*, π_L^*
1^1A_2	75	n_{H-1}	π_L^*	49	n_{H-1}	π_L^*	45	n_{H-1}	π_L^*
	16	n_H	π_{L+1}^*	14	n_H	π_{L+1}^*	17	n_H	π_{L+1}^*
	3	π_{H-2}, n_H	π_L^*, π_L^*				2	π_{H-2}, n_H	π_L^*, π_L^*
1^1B_2	88	π_{H-2}	π_L^*	58	π_{H-2}	π_L^*	56	π_{H-2}	π_L^*
	4	π_{H-3}, π_{H-2}	π_L^*, π_L^*	4	π_{H-3}, π_{H-2}	π_L^*, π_L^*	5	π_{H-3}, π_{H-2}	π_L^*, π_L^*
				2	π_{H-3}	π_{L+1}^*	2	π_{H-3}	π_{L+1}^*
							2	π_{H-7}, π_{H-2}	π_L^*, π_{L+1}^*
2^1A_2	61	n_H	π_{L+1}^*	35	n_H	π_{L+1}^*	29	n_H	π_{L+1}^*
	11	n_{H-1}	π_L^*	9	n_{H-1}	π_L^*	10	n_{H-1}	π_L^*
	9	π_{H-2}, n_{H-1}	π_L^*, π_{L+1}^*	7	π_{H-2}, n_H	π_L^*, π_L^*	10	π_{H-2}, n_H	π_L^*, π_L^*
	8	π_{H-2}, n_H	π_L^*, π_L^*	7	π_{H-2}, n_{H-1}	π_L^*, π_{L+1}^*	8	π_{H-2}, n_{H-1}	π_L^*, π_{L+1}^*
2^1A_1	86	n_{H-1}, n_H	π_L^*, π_{L+1}^*						
2^1B_1	63	n_{H-1}	π_{L+1}^*	36	n_{H-1}	π_{L+1}^*	30	n_{H-1}	π_{L+1}^*
	11	π_{H-2}, n_H	π_L^*, π_{L+1}^*	7	π_{H-2}, n_H	π_L^*, π_{L+1}^*	9	π_{H-2}, n_{H-1}	π_L^*, π_L^*
	7	π_{H-2}, n_{H-1}	π_L^*, π_L^*	7	π_{H-2}, n_{H-1}	π_L^*, π_L^*	9	π_{H-2}, n_H	π_L^*, π_{L+1}^*
	6	n_H	π_L^*	6	n_H	π_L^*	7	n_H	π_L^*
5^1A_1	49	n_H, n_H	π_L^*, π_L^*	32	n_H, n_H	π_L^*, π_L^*	31	n_H, n_H	π_L^*, π_L^*
	37	n_{H-1}, n_{H-1}	π_L^*, π_L^*	25	n_{H-1}, n_{H-1}	π_L^*, π_L^*	25	n_{H-1}, n_{H-1}	π_L^*, π_L^*
1^3B_1	82	n_H	π_L^*	53	n_H	π_L^*	51	n_H	π_L^*
	12	n_{H-1}	π_{L+1}^*	12	n_{H-1}	π_{L+1}^*	13	n_{H-1}	π_{L+1}^*
1^3A_2	76	n_{H-1}	π_L^*	49	n_{H-1}	π_L^*	46	n_{H-1}	π_L^*
	18	n_H	π_{L+1}^*	15	n_H	π_{L+1}^*	17	n_H	π_{L+1}^*
				2	n_H	Ry_{L+5}			
1^3B_2	88	π_{H-2}	π_L^*	59	π_{H-2}	π_L^*	57	π_{H-2}	π_L^*
	8	π_{H-3}	π_{L+1}^*	8	π_{H-3}	π_{L+1}^*	10	π_{H-3}	π_{L+1}^*
1^3A_1	58	π_{H-3}	π_L^*	43	π_{H-3}	π_L^*	39	π_{H-3}	π_L^*
	36	π_{H-2}	π_{L+1}^*	23	π_{H-2}	π_{L+1}^*	26	π_{H-2}	π_{L+1}^*
				2	π_{H-2}	Ry_{L+5}			
2^3B_2	87	n_{H-1}, n_H	π_L^*, π_L^*	58	n_{H-1}, n_H	π_L^*, π_L^*	56	n_{H-1}, n_H	π_L^*, π_L^*
	6	n_{H-1}, n_H	π_{L+1}^*, π_{L+1}^*	5	n_{H-1}, n_H	π_{L+1}^*, π_{L+1}^*	7	n_{H-1}, n_H	π_{L+1}^*, π_{L+1}^*
2^3A_1	89	n_{H-1}, n_H	π_L^*, π_{L+1}^*	57	n_{H-1}, n_H	π_L^*, π_{L+1}^*	57	n_{H-1}, n_H	π_L^*, π_{L+1}^*
2^3A_2	65	n_H	π_{L+1}^*	33	n_H	π_{L+1}^*	30	n_H	π_{L+1}^*
	15	n_{H-1}	π_L^*	10	n_{H-1}	π_L^*	11	n_{H-1}	π_L^*
2^3B_1	69	n_{H-1}	π_{L+1}^*	35	n_{H-1}	π_{L+1}^*	32	n_{H-1}	π_{L+1}^*

Continued on next page

Table S52 – continued from previous page

DFT/MRCI				MRMP2			MRMP2		
(BH-LYP)				(HF)			(BH-LYP)		
Excitation				Excitation			Excitation		
State	%	from	to	%	from	to	%	from	to
	9	n_H	π_L^*	9	π_{H-2}, n_H	π_L^*, π_{L+1}^*	10	π_{H-2}, n_H	π_L^*, π_{L+1}^*
	8	π_{H-2}, n_H	π_L^*, π_{L+1}^*	7	n_H	π_L^*	8	n_H	π_L^*

The orbitals presented in the table are labeled according to the order obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different:

The n_H bh-lyp orbital corresponds to the n_{H-1} hf orbital;

The n_{H-1} bh-lyp orbital corresponds to the n_{H-2} hf orbital;

The π_{H-2} bh-lyp orbital corresponds to the π_H hf orbital.

Table S53.: Calculated percentage of electron configurations in the excited states wave functions of **dithiosuccinimide** obtained at the DFT/MRCI, and DFT/MRCI-R levels of theory. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			DFT/MRCI-R		
	%	Excitation		%	Excitation	
		from	to		from	to
1^1B_1	81	n_H	π_L^*	82	n_H	π_L^*
	11	n_{H-1}	π_{L+1}^*	10	n_{H-1}	π_{L+1}^*
1^1A_2	75	n_{H-1}	π_L^*	75	n_{H-1}	π_L^*
	16	n_H	π_{L+1}^*	16	n_H	π_{L+1}^*
	3	π_{H-2}, n_H	π_L^*, π_L^*	3	π_{H-2}, n_H	π_L^*, π_L^*
1^1B_2	88	π_{H-2}	π_L^*	87	π_{H-2}	π_L^*
	4	π_{H-3}, π_{H-2}	π_L^*, π_L^*	5	π_{H-3}, π_{H-2}	π_L^*, π_L^*
2^1A_2	61	n_H	π_{L+1}^*	59	n_H	π_{L+1}^*
	11	n_{H-1}	π_L^*	12	π_{H-2}, n_{H-1}	π_L^*, π_{L+1}^*
	9	π_{H-2}, n_{H-1}	π_L^*, π_{L+1}^*	10	n_{H-1}	π_L^*
	8	π_{H-2}, n_H	π_L^*, π_L^*	6	π_{H-2}, n_H	π_L^*, π_L^*
2^1A_1	86	n_{H-1}, n_H	π_L^*, π_{L+1}^*	87	n_{H-1}, n_H	π_L^*, π_{L+1}^*
2^1B_1	63	n_{H-1}	π_{L+1}^*	60	n_{H-1}	π_{L+1}^*
	11	π_{H-2}, n_H	π_L^*, π_{L+1}^*	16	π_{H-2}, n_H	π_L^*, π_{L+1}^*
	7	π_{H-2}, n_{H-1}	π_L^*, π_L^*	6	π_{H-2}, n_{H-1}	π_L^*, π_L^*
	6	n_H	π_L^*	7	n_H	π_L^*
5^1A_1	49	n_H, n_H	π_L^*, π_L^*	49	n_H, n_H	π_L^*, π_L^*
	37	n_{H-1}, n_{H-1}	π_L^*, π_L^*	34	n_{H-1}, n_{H-1}	π_L^*, π_L^*
1^3B_1	82	n_H	π_L^*	82	n_H	π_L^*
	12	n_{H-1}	π_{L+1}^*	11	n_{H-1}	π_{L+1}^*
1^3A_2	76	n_{H-1}	π_L^*	76	n_{H-1}	π_L^*
	18	n_H	π_{L+1}^*	17	n_H	π_{L+1}^*
1^3B_2	88	π_{H-2}	π_L^*	89	π_{H-2}	π_L^*
	8	π_{H-3}	π_{L+1}^*	7	π_{H-3}	π_{L+1}^*
1^3A_1	58	π_{H-3}	π_L^*	58	π_{H-3}	π_L^*
	36	π_{H-2}	π_{L+1}^*	36	π_{H-2}	π_{L+1}^*
2^3B_2	87	n_{H-1}, n_H	π_L^*, π_L^*	85	n_{H-1}, n_H	π_L^*, π_L^*
	6	n_{H-1}, n_H	π_{L+1}^*, π_{L+1}^*	6	n_{H-1}, n_H	π_{L+1}^*, π_{L+1}^*
2^3A_1	89	n_{H-1}, n_H	π_L^*, π_{L+1}^*	87	n_{H-1}, n_H	π_L^*, π_{L+1}^*
2^3A_2	65	n_H	π_{L+1}^*	59	n_H	π_{L+1}^*
	15	n_{H-1}	π_L^*	12	n_{H-1}	π_L^*
2^3B_1	69	n_{H-1}	π_{L+1}^*	60	n_{H-1}	π_{L+1}^*
	9	n_H	π_L^*	6	n_H	π_L^*
	8	π_{H-2}, n_H	π_L^*, π_{L+1}^*	17	π_{H-2}, n_H	π_L^*, π_{L+1}^*

S4.14. *Methionine*Table S54. Computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of **methionine**. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)			
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)
2^1A	$\pi \rightarrow \sigma^*/Ry$	5.12 (0)	5.32 (0)	5.99 (0) ¹	5.24 (0)
3^1A	$n_O \rightarrow \pi^*$	5.48 (0.002)	5.71 (0.003)	5.97 (0.002) ²	5.54 (0.002)
1^3A	$\pi \rightarrow \sigma^*/Ry$	4.65	4.94	5.62	4.77
2^3A	$n_O \rightarrow \pi^*$	5.13	5.46	5.77	5.26
3^3A	$\pi \rightarrow \sigma^*/Ry$	5.74	6.00	6.74	5.74
4^3A	$\pi_{H-4} \rightarrow \pi^*$	6.06	6.31	7.01 ³	6.24 ¹
MRMP2(HF): ¹ 3^1A , ² 2^1A , ³ 7^3A					
MRMP2(BH-LYP): ¹ 6^3A					

Table S55.: Calculated percentage of electron configurations in the excited states wave functions of **methionine** obtained at the DFT/MRCI, MRMP2(HF) and MRMP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF) [†]			(BH-LYP)		
	Excitation			Excitation			Excitation		
	%	from	to	%	from	to	%	from	to
2 ¹ A	44	π_H	$(\sigma^*/Ry)_{L+1}$	25	π_H	$(\sigma^*/Ry)_{L+1}$	29	π_H	$(\sigma^*/Ry)_{L+1}$
	20	π_H	$(\sigma^*/Ry)_{L+2}$	13	π_H	$(Ry/\sigma^*)_{L+2}$	16	π_H	$(\sigma^*/Ry)_{L+2}$
	13	π_H	$(Ry/\sigma^*)_{L+3}$	7	π_H	$(Ry/\sigma^*)_{L+6}$	8	π_H	$(Ry/\sigma^*)_{L+3}$
	5	π_H	$(Ry)_{L+4}$	7	π_H	$(\sigma^*/Ry)_{L+9}$			
				5	π_H	$(Ry/\sigma^*)_{L+5}$			
3 ¹ A	61	$n(O)_{H-2}$	π_L^*	28	$n(O)_{H-3}$	π_{L+3}^*	48	$n(O)_{H-2}$	π_L^*
	7	$n(O)_{H-2}$	$(\sigma^*/Ry)_{L+1}$	18	$n(O)_{H-3}$	$(Ry)_{L+4}$			
	7	$n(S)_{H-3}$	π_L^*	6	$n(O)_{H-3}$	$(Ry/\sigma^*)_{L+5}$			
	5	$n(N)_{H-1}$	π_L^*						
1 ³ A	42	π_H	$(\sigma^*/Ry)_{L+1}$	24	π_H	$(\sigma^*/Ry)_{L+1}$	29	π_H	$(\sigma^*/Ry)_{L+1}$
	20	π_H	$(\sigma^*/Ry)_{L+2}$	13	π_H	$(Ry/\sigma^*)_{L+2}$	15	π_H	$(\sigma^*/Ry)_{L+2}$
	13	π_H	$(Ry/\sigma^*)_{L+3}$	8	π_H	$(Ry/\sigma^*)_{L+6}$	8	π_H	$(Ry/\sigma^*)_{L+3}$
	6	π_H	$(Ry)_{L+4}$	8	π_H	$(\sigma^*/Ry)_{L+9}$			
				6	π_H	$(Ry/\sigma^*)_{L+5}$			
2 ³ A	63	$n(O)_{H-2}$	π_L^*	29	$n(O)_{H-3}$	π_{L+3}^*	50	$n(O)_{H-2}$	π_L^*
	7	$n(O)_{H-2}$	$(\sigma^*/Ry)_{L+1}$	18	$n(O)_{H-3}$	$(Ry)_{L+4}$			
	7	$n(S)_{H-3}$	π_L^*	6	$n(O)_{H-3}$	$(Ry/\sigma^*)_{L+5}$			
	5	$n(N)_{H-1}$	π_L^*						
3 ³ A	33	π_H	π_L^*	15	π_H	$(Ry/\sigma^*)_{L+8}$	29	π_H	$(\sigma^*/Ry)_{L+7}$
	26	π_H	$(\sigma^*/Ry)_{L+7}$	13	π_H	$(Ry)_L$	11	π_H	$(Ry/\sigma^*)_{L+5}$
	12	π_H	$(Ry/\sigma^*)_{L+5}$	10	π_H	$(\sigma^*/Ry)_{L+9}$	8	π_H	π_L^*
	10	π_H	$(\sigma^*/Ry)_{L+2}$	8	π_H	$(Ry/\sigma^*)_{L+7}$	7	π_H	$(\sigma^*/Ry)_{L+2}$
4 ³ A	70	π_{H-4}	π_L^*	26	π_{H-4}	π_{L+3}^*	49	π_{H-4}	π_L^*
	8	π_{H-4}	$(\sigma^*/Ry)_{L+1}$	18	π_{H-4}	$(Ry)_{L+4}$			
				6	π_{H-4}	$(Ry/\sigma^*)_{L+5}$			
				5	σ_{H-5}	π_{L+3}^*			

[†] Since the BH-LYP virtual orbitals are very different compared to the HF orbitals for Methionine, in the table are presented HF orbitals in original ordering, without correlation with BH-LYP orbitals

Regarding the occupied orbitals, the $n(O)_{H-2}$ bh-lyp orbital corresponds to the $n(O)_{H-3}$ hf orbital;

S4.15. IsoalloxazineTable S56. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of **isoalloxazine**. The oscillator strengths are given in the parentheses.

State	Dominant character	Energies(eV)				Experiment
		DFT/MRCI	DFT/MRCI-R	MRMP2 (HF)	MRMP2 (BH-LYP)	
$2^1A'$	$\pi \rightarrow \pi^*$	3.03 (0.287)	3.00 (0.311)	2.84 (0.230)	2.64 (0.253)	2.85^a
$1^1A''$	$n \rightarrow \pi^*$	3.16 (0.002)	3.28 (0.002)	3.52 (0) ¹	3.85 (0) ¹	
$2^1A''$	$n \rightarrow \pi^*$	3.34 (0.001)	3.46 (0.001)	3.45 (0.002) ²	3.11 (0.002) ²	
$3^1A''$	$n \rightarrow \pi^*$	3.90 (0)	4.00 (0)	3.87 (0)	3.76 (0) ³	
$3^1A'$	$\pi \rightarrow \pi^*$	3.94 (0.194)	3.94 (0.188)	3.98 (0.097)	3.71 (0.143) ⁴	3.76 ^a
$1^3A'$	$\pi \rightarrow \pi^*$	2.31	2.27	2.60	2.29	
$1^3A''$	$n \rightarrow \pi^*$	2.86	3.01	3.53	2.98	
$2^3A'$	$\pi \rightarrow \pi^*$	3.12	3.13	3.31	2.84	
$2^3A''$	$n \rightarrow \pi^*$	3.19	3.28	3.87	3.61 ⁵	

MRMP2(HF): $1^2A''$, $2^1A''$ MRMP2(BHLYP): $1^4A''$, $2^1A''$, $3^2A''$, $4^6A'$, $5^3A''$ ^a 8-methylisoalloxazine in ethanol [28]

Table S57.: Calculated percentage of electron configurations in the excited states wave functions of **isoalloxazine** obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

State	DFT/MRCI			MRMP2			MRMP2		
	(BH-LYP)			(HF)			(BH-LYP)		
	%	Excitation		%	Excitation		%	Excitation	
		from	to		from	to		from	to
$2^1A'$	83	π_H	π_L^*	48	π_H	π_L^*	45	π_H	π_L^*
				2	π_{H-1}	π_{L+1}^*	2	π_{H-1}	π_{L+1}^*
				2	π_{H-1}	π_L^*			
$1^1A''$	50	$n(O)_{H-2}$	π_L^*	36	$n(O)_{H-2}$	π_L^*	32	$n(O)_{H-2}$	π_L^*
	27	$n(N)_{H-4}$	π_L^*	4	$n(N)_{H-4}$	π_L^*	7	$n(O)_{H-5}$	π_L^*
	2	$n(N)_{H-7}$	π_L^*	2	$n(O)_{H-5}$	π_L^*	3	$n(O)_{H-2}$	π_{L+4}^*
				2	$n(O)_{H-5}$	π_{L+4}^*	2	$n(O)_{H-5}$	π_{L+4}^*
				2	$n(N)_{H-4}$	π_{L+4}^*	2	$n(N)_{H-4}$	π_L^*
$2^1A''$	45	$n(N)_{H-4}$	π_L^*	40	$n(N)_{H-4}$	π_L^*	37	$n(N)_{H-4}$	π_L^*
	21	$n(O)_{H-2}$	π_L^*	7	$n(N)_{H-7}$	π_L^*	7	$n(N)_{H-7}$	π_L^*
	8	$n(O)_{H-5}$	π_L^*	2	$n(O)_{H-2}$	π_L^*	5	$n(O)_{H-2}$	π_L^*
	5	$n(N)_{H-7}$	π_L^*	2	$n(N)_{H-4}$	π_{L+2}^*			
$3^1A'$	74	π_{H-1}	π_L^*	43	π_{H-1}	π_L^*	41	π_{H-1}	π_L^*
	4	π_H	π_{L+1}^*	5	π_H	π_{L+1}^*	4	π_H	π_{L+1}^*
	2	π_H	π_{L+4}^*	3	π_H	π_L^*	2	π_H	π_L^*
				2	π_H	π_{L+2}^*	2	π_H	π_{L+2}^*
$1^3A'$	85	π_H	π_L^*	45	π_H	π_L^*	43	π_H	π_L^*
	4	π_{H-1}	π_L^*	7	π_{H-1}	π_L^*	7	π_{H-1}	π_L^*
$1^3A''$	56	$n(N)_{H-4}$	π_L^*	36	$n(N)_{H-4}$	π_L^*	34	$n(N)_{H-4}$	π_L^*
	17	$n(O)_{H-2}$	π_L^*	11	$n(N)_{H-7}$	π_L^*	11	$n(N)_{H-7}$	π_L^*
	10	$n(N)_{H-7}$	π_L^*				5	$n(O)_{H-2}$	π_L^*
$2^3A''$	53	$n(O)_{H-2}$	π_L^*	29	$n(O)_{H-2}$	π_L^*	32	$n(O)_{H-2}$	π_L^*
	10	$n(N)_{H-4}$	π_L^*	7	$n(O)_{H-5}$	π_L^*	7	$n(O)_{H-5}$	π_L^*
	10	$n(O)_{H-5}$	π_L^*	4	$n(N)_{H-4}$	π_L^*	4	$n(O)_{H-2}$	π_{L+4}^*
	3	$n(O)_{H-2}$	π_{L+4}^*	4	$n(O)_{H-5}$	π_{L+4}^*	3	$n(O)_{H-5}$	π_{L+4}^*
	3	$n(N)_{H-7}$	π_L^*	4	$n(N)_{H-4}$	π_{L+4}^*			
	3	$n(O)_{H-5}$	π_{L+4}^*	2	$n(O)_{H-2}$	π_{L+4}^*			

The orbitals presented in the table are labeled according to the order obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different:

The $n(O)_{H-2}$ bh-lyp orbital corresponds to the $n(O)_{H-4}$ hf orbital;

The $n(N)_{H-4}$ bh-lyp orbital corresponds to the $n(N)_{H-5}$ hf orbital;

The $n(O)_{H-5}$ bh-lyp orbital corresponds to the $n(O)_{H-6}$ hf orbital.

The π_{L+4}^* bh-lyp orbital corresponds to the π_{L+6}^* hf orbital.

Table S58. Isoalloxazine, SOMEs, RAS 16-11-2

	SOMEs(cm^{-1})		
	DFT/MRCI	MRMP2 (HF)	MRMP2 (BH-LYP)
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } x} 1^1 A' \rangle$	8.5	11.4	12.1
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } x} 2^1 A' \rangle$	6.0	3.1	3.0
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } x} 3^1 A' \rangle$	4.2	3.6	3.6
$\langle 2^3 A'' \hat{\mathcal{H}}_{\text{SO } x} 1^1 A' \rangle$	10.3	6.8	7.2
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } y} 1^1 A' \rangle$	10.7	3.6	4.7
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } y} 2^1 A' \rangle$	2.0	0.4	0.3
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } y} 3^1 A' \rangle$	2.5	1.7	1.8
$\langle 2^3 A'' \hat{\mathcal{H}}_{\text{SO } y} 1^1 A' \rangle$	23.0	24.7	25.7
$\langle 1^3 A' \hat{\mathcal{H}}_{\text{SO } x} 1^1 A'' \rangle$	11.1	2.4	0.9
$\langle 1^3 A' \hat{\mathcal{H}}_{\text{SO } x} 2^1 A'' \rangle$	2.4	7.4	7.8
$\langle 1^3 A' \hat{\mathcal{H}}_{\text{SO } y} 1^1 A'' \rangle$	9.7	8.3	9.0
$\langle 1^3 A' \hat{\mathcal{H}}_{\text{SO } y} 2^1 A'' \rangle$	7.3	2.3	3.1
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } z} 1^1 A'' \rangle$	1.9	4.8	5.6
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } z} 2^1 A'' \rangle$	3.2	0.5	0.8
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } x} 1^3 A' \rangle$	9.7	6.9	7.1
$\langle 1^3 A'' \hat{\mathcal{H}}_{\text{SO } y} 1^3 A' \rangle$	4.4	1.8	2.1
$\langle 2^3 A'' \hat{\mathcal{H}}_{\text{SO } x} 1^3 A' \rangle$	2.3	1.6	1.7
$\langle 2^3 A'' \hat{\mathcal{H}}_{\text{SO } y} 1^3 A' \rangle$	10.3	8.1	8.3
$\langle 2^3 A'' \hat{\mathcal{H}}_{\text{SO } z} 1^3 A'' \rangle$	4.2	5.9	5.9

S5. Optimized geometries of all polyatomic molecules in Turbomole format

o-benzyne

```

$coord
  1.17436585005558      0.00000000000000      -2.91783955856904      c
 -1.17436585005558      0.00000000000000      -2.91783955856904      c
 -2.75209598591275      0.00000000000000      -0.84138302133317      c
 -1.32564422167504      0.00000000000000      1.40629603021343      c
  1.32564422167504      0.00000000000000      1.40629603021343      c
  2.75209598591275      0.00000000000000      -0.84138302133317      c
 -4.79588042002593      0.00000000000000      -0.84670344838957      h
 -2.31805929976997      0.00000000000000      3.19962999807835      h
  2.31805929976997      0.00000000000000      3.19962999807835      h
  4.79588042002593      0.00000000000000      -0.84670344838957      h
$user-defined bonds
$end

```

#####

Formaldehyde

```

$coord
  0.00000000000000      0.00000000000000      -1.13492173758470      c
  0.00000000000000      0.00000000000000      1.13487499210216      o
  0.00000000000000      1.77442119446536      -2.24490992799825      h
  0.00000000000000      -1.77442119446536      -2.24490992799825      h
$user-defined bonds
$end

```

#####

Thioformaldehyde

```

$coord
  0.00000000000000      0.00000000000000      -0.21272080063682      c
  0.00000000000000      0.00000000000000      2.83208049504587      s
 -1.74201265716538      0.00000000000000      -1.30967984720453      h
  1.74201265716538      0.00000000000000      -1.30967984720453      h
$user-defined bonds
$end

```

#####

Furan

\$coord

0.0000000000000000	0.0000000000000000	-2.60951767812713	o
-2.06944695013647	0.0000000000000000	-1.07409817620120	c
-1.35446631345745	0.0000000000000000	1.38655862649115	c
2.06944695013647	0.0000000000000000	-1.07409817620120	c
1.35446631345745	0.0000000000000000	1.38655862649115	c
-3.87275264412434	0.0000000000000000	-2.01429504621195	h
-2.58841049419110	0.0000000000000000	3.00661787535332	h
2.58841049419110	0.0000000000000000	3.00661787535332	h
3.87275264412434	0.0000000000000000	-2.01429504621195	h

\$user-defined bonds

\$end

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Thiophene

\$coord

1.34566119550646	0.0000000000000000	-2.48135783630059	c
-1.34566119550646	0.0000000000000000	-2.48135783630059	c
-2.34140829359619	0.0000000000000000	-0.10207603421092	c
2.34140829359619	0.0000000000000000	-0.10207603421092	c
0.0000000000000000	0.0000000000000000	2.16998967240478	s
-4.30322604139690	0.0000000000000000	0.44859441791091	h
-2.48480316694106	0.0000000000000000	-4.17813269206495	h
2.48480316694106	0.0000000000000000	-4.17813269206495	h
4.30322604139690	0.0000000000000000	0.44859441791091	h

\$user-defined bonds

\$end

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Quinoxaline

coord

0.0000000000000000	1.34851448928290	-0.04308396822032	c
0.0000000000000000	-1.34851448928290	-0.04308396822032	c
0.0000000000000000	2.65971823554233	2.28673743415383	c
0.0000000000000000	1.33705869093915	4.51645111448426	c
0.0000000000000000	-1.33705869093915	4.51645111448426	c
0.0000000000000000	-2.65971823554233	2.28673743415383	c
0.0000000000000000	-2.67165472069636	-2.25056228491017	n
0.0000000000000000	2.67165472069636	-2.25056228491017	n
0.0000000000000000	1.33982622873228	-4.33893321844487	c
0.0000000000000000	-1.33982622873228	-4.33893321844487	c
0.0000000000000000	2.36641046716173	-6.11641565124786	h
0.0000000000000000	-2.36641046716173	-6.11641565124786	h
0.0000000000000000	4.70524646880327	2.23830739016897	h
0.0000000000000000	2.34078894813222	6.30069856802307	h
0.0000000000000000	-2.34078894813222	6.30069856802307	h
0.0000000000000000	-4.70524646880327	2.23830739016897	h

\$user-defined bonds

\$end

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Quinazoline

\$coord

-1.36377830593764	0.02164891624333	0.0000000000000000	c
1.32358004466339	-0.00642782560434	0.0000000000000000	c
-2.67344557760090	2.35111102112969	0.0000000000000000	c
-1.34210560585668	4.57650051698381	0.0000000000000000	c
1.33118157888386	4.55054284673907	0.0000000000000000	c
2.64773551616107	2.31460626473841	0.0000000000000000	c
2.62027853734640	-2.23232554321978	0.0000000000000000	n
-2.55361790292543	-2.37354727839355	0.0000000000000000	c
-1.29008728275860	-4.50630971662982	0.0000000000000000	n
1.27443449300352	-4.30859688746912	0.0000000000000000	c
-4.60660305711199	-2.49662580101590	0.0000000000000000	h
2.29583861341275	-6.08655825695464	0.0000000000000000	h
-4.72287386788293	2.35172083639553	0.0000000000000000	h
-2.33128955432688	6.36844044222261	0.0000000000000000	h
2.34668983885953	6.32863938189363	0.0000000000000000	h
4.69249305982863	2.26136784419168	0.0000000000000000	h

\$user-defined bonds

\$end

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Pyranthione

\$coord

0.0000000000000000	0.0000000000000000	-5.41280084911143	s
0.0000000000000000	0.0000000000000000	-2.27610234375952	c
2.28239911071821	0.0000000000000000	-0.77097741589196	c
-2.28239911071821	0.0000000000000000	-0.77097741589196	c
2.19281770453302	0.0000000000000000	1.76800159282312	c
-2.19281770453302	0.0000000000000000	1.76800159282312	c
0.0000000000000000	0.0000000000000000	3.10029625536432	o
4.09779134136361	0.0000000000000000	-1.70846637180746	h
-4.09779134136361	0.0000000000000000	-1.70846637180746	h
3.81569058976344	0.0000000000000000	3.00574566362965	h
-3.81569058976344	0.0000000000000000	3.00574566362965	h

\$user-defined bonds

\$end

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Dithiin

\$coord

-2.86580686520235	0.06685457466165	-0.58761113643798	c
-1.74686625152159	-0.93439975340578	-3.58743246371355	s
1.74686625152159	0.93439975340578	-3.58743246371355	s
2.86580686520235	-0.06685457466165	-0.58761113643798	c
1.34949386294333	-0.26465201376855	1.43325076748021	c
-1.34949386294333	0.26465201376855	1.43325076748021	c
4.88043546579430	-0.42046691325140	-0.47732257370807	h
2.19170307049153	-0.81587368262624	3.21985735926151	h
-2.19170307049153	0.81587368262624	3.21985735926151	h
-4.88043546579430	0.42046691325140	-0.47732257370807	h

\$user-defined bonds

\$end

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Bithiophene

coord

-3.96988778421768	1.08891220762545	0.86140126635055	s
-0.74152793302954	1.15246315166230	0.17136717343972	c
0.02013601870388	3.59049859122632	-0.30037764090575	c
-1.96658915178120	5.38569505078307	-0.13126800701727	c
-4.23600721856751	4.31664305664117	0.46548485545081	c
0.74152793302954	-1.15246315166230	0.17136717343972	c
-0.02013601870388	-3.59049859122632	-0.30037764090575	c
1.96658915178120	-5.38569505078307	-0.13126800701727	c
4.23600721856751	-4.31664305664117	0.46548485545081	c
3.96988778421768	-1.08891220762545	0.86140126635055	s
6.04440759167992	-5.22731659581586	0.69687312532149	h
-6.04440759167992	5.22731659581586	0.69687312532149	h
-1.71756381233833	7.38826074025362	-0.45753873320741	h
1.94373787470285	4.07268383409784	-0.79726048539097	h
-1.94373787470285	-4.07268383409784	-0.79726048539097	h
1.71756381233833	-7.38826074025362	-0.45753873320741	h

\$user-defined bonds

\$end

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Nitromethane

\$coord

1.39335214705160	-0.76295979932813	0.00000000000000	n
1.28450387612169	-3.06825847571066	0.00000000000000	o
3.32868182243600	0.49273279279710	0.00000000000000	o
-1.08606004843182	0.62725172762346	0.00000000000000	c
-0.69904605232834	2.63955977340387	0.00000000000000	h
-2.11071587242454	0.03583699060714	-1.68078913533078	h
-2.11071587242454	0.03583699060714	1.68078913533078	h

\$user-defined bonds

\$end

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Nitrobenzene

\$coord

0.000000000000000	0.000000000000000	1.60347294530390	c
0.000000000000000	0.000000000000000	-3.59896025534619	c
2.29878831137124	0.000000000000000	0.33655081995768	c
-2.29878831137124	0.000000000000000	0.33655081995768	c
-2.28322846111443	0.000000000000000	-2.28896805815391	c
2.28322846111443	0.000000000000000	-2.28896805815391	c
4.04004564954374	0.000000000000000	1.40275883089641	h
-4.04004564954374	0.000000000000000	1.40275883089641	h
-4.05541523981593	0.000000000000000	-3.31160564246933	h
4.05541523981593	0.000000000000000	-3.31160564246933	h
0.000000000000000	0.000000000000000	-5.64617215317262	h
0.000000000000000	0.000000000000000	4.40465230335952	n
2.04887036382285	0.000000000000000	5.47976762969691	o
-2.04887036382285	0.000000000000000	5.47976762969691	o

\$user-defined bonds

\$end

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Dithiosuccinimide

\$coord

0.000000000000000	-1.45666900594610	-1.66620418588077	c
0.000000000000000	-2.21034538961508	1.10066498364750	c
0.000000000000000	0.000000000000000	2.46084368279514	n
0.000000000000000	2.21034538961508	1.10066498364750	c
0.000000000000000	1.45666900594610	-1.66620418588077	c
0.000000000000000	5.04724275757076	2.32512196784998	s
0.000000000000000	-5.04724275757076	2.32512196784998	s
0.000000000000000	0.000000000000000	4.37458631463165	h
1.65477054116251	-2.26812361781069	-2.58864888216505	h
-1.65477054116251	-2.26812361781069	-2.58864888216505	h
-1.65477054116251	2.26812361781069	-2.58864888216505	h
1.65477054116251	2.26812361781069	-2.58864888216505	h

\$user-defined bonds

\$end

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Methionine

\$coord

4.76099430895915	-1.71333782672988	1.79001120037847	c
4.44195060765592	-2.57337548311441	4.17681740779049	o
6.73547550894334	-0.87343024066359	1.03129552889427	o
6.03384721355275	-2.33959388425558	5.05836468986696	h
2.33223111761168	-1.83336199077757	0.26252246897826	c
3.01191601137541	-2.24565242658838	-2.37088018598580	n
1.25452267943939	-3.46488828582037	0.93136353597730	h
0.78326112962969	0.59026860172462	0.85795464483749	c
1.50001951379748	-2.08106869788800	-3.52885842715726	h
4.36762180027747	-1.00791439640966	-2.92238815854439	h
-1.82234113037246	0.55764684457247	-0.37825550229080	c
0.55704472603565	0.75684654251706	2.90554979877657	h
1.85046680753457	2.23982186123099	0.21438436052467	h
-3.58938225022865	3.40382269096334	0.48331018053293	s
-1.66355429116183	0.50012898279821	-2.43637847953666	h
-2.88850199322567	-1.10159950300212	0.23926972954955	h
-6.46776499311525	2.85263434307328	-1.31680416127601	c
-7.71857857571236	4.44536166753883	-0.94532193712846	h
-6.07612816129063	2.77019011069814	-3.33892928668144	h
-7.40310002970565	1.11750109013264	-0.71302740750607	h

\$user-defined bonds

\$end

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Isoalloxazine

\$coord

2.51988147835166	-1.36384049945196	0.00000000000000	c
4.57172112766037	-2.70142876166231	0.00000000000000	n
6.87887313585653	-1.46785020644587	0.00000000000000	c
6.85196359523531	1.21173040580103	0.00000000000000	n
4.79189986631520	2.81261547442180	0.00000000000000	c
2.33542437604255	1.39534955869551	0.00000000000000	c
0.24197822755524	-2.58712143575286	0.00000000000000	n
-2.05105524911613	-1.36512882582954	0.00000000000000	c
-2.00997620849890	1.31100618503416	0.00000000000000	c
0.22684912824209	2.62521091683690	0.00000000000000	n
-4.35206876488726	-2.66514536632553	0.00000000000000	c
-6.58317892927744	-1.30417219401142	0.00000000000000	c
-6.57340285963868	1.34837992430289	0.00000000000000	c
-4.30974932946563	2.63989017414723	0.00000000000000	c
8.88925948139859	-2.55529606892658	0.00000000000000	o
4.97576345077364	5.09131875662744	0.00000000000000	o
-8.34351156204724	2.37249377528319	0.00000000000000	h
0.32588952491405	-4.50054276596776	0.00000000000000	h
-8.36597009104112	-2.30989604609086	0.00000000000000	h
-4.37233213191804	-4.71294314907122	0.00000000000000	h
-4.22485476781693	4.68341199676864	0.00000000000000	h
8.57651329975121	2.04188095074323	0.00000000000000	h

\$user-defined bonds

\$end

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