

Supporting Information:  
The semi-experimental approach at work:  
Equilibrium structure of radical species

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## Standard deviations of the LSQ fits

**Table S1: Standard deviations of the LSQ fits for the  $r_0$ ,  $r_e(\text{SE})$ , and  $r_e(\text{SE})_{full}$  structures reported in the main text. Units:  $u \cdot a_0$**

Molecule	$r_0$	$r_e(\text{SE})$	$r_e(\text{SE})_{full}$
NH	$2.12 \times 10^{-4}$	$4.69 \times 10^{-6}$	$6.68 \times 10^{-7}$
PH	$4.66 \times 10^{-4}$	$7.83 \times 10^{-6}$	$1.86 \times 10^{-6}$
AsH	$9.73 \times 10^{-5}$	$1.67 \times 10^{-7}$	$1.28 \times 10^{-5}$
SO	$2.144 \times 10^{-5}$	$2.81 \times 10^{-7}$	$9.05 \times 10^{-8}$
BO	$5.31 \times 10^{-6}$	$4.28 \times 10^{-6}$	$2.85 \times 10^{-8}$
CH	$2.83 \times 10^{-8}$	$2.18 \times 10^{-9}$	$1.91 \times 10^{-11}$
CN	$1.21 \times 10^{-5}$	$7.37 \times 10^{-6}$	$7.95 \times 10^{-6}$
SH	$3.01 \times 10^{-4}$	$7.37 \times 10^{-7}$	$1.64 \times 10^{-7}$
OH	$1.55 \times 10^{-4}$	$2.53 \times 10^{-6}$	$1.84 \times 10^{-5}$
NS	$7.35 \times 10^{-6}$	$7.51 \times 10^{-7}$	$9.8 \times 10^{-7}$
NO	$9.24 \times 10^{-6}$	$8.29 \times 10^{-5}$	$8.27 \times 10^{-5}$
CH <sub>2</sub>	$1.35 \times 10^{-3}$	$9.00 \times 10^{-4}$	$8.99 \times 10^{-4}$
NH <sub>2</sub>	$4.76 \times 10^{-6}$	$2.25 \times 10^{-6}$	$5.05 \times 10^{-9}$
PH <sub>2</sub>	$3.03 \times 10^{-5}$	$7.86 \times 10^{-6}$	$2.51 \times 10^{-6}$
AsH <sub>2</sub>	$5.39 \times 10^{-4}$	$2.56 \times 10^{-6}$	$3.03 \times 10^{-7}$
CCS	$2.71 \times 10^{-5}$	$4.25 \times 10^{-8}$	$1.72 \times 10^{-8}$
HCO	$1.18 \times 10^{-5}$	$9.82 \times 10^{-6}$	$2.25 \times 10^{-6}$
HCS	$2.32 \times 10^{-4}$	$1.01 \times 10^{-4}$	$9.89 \times 10^{-5}$
HSC	$2.03 \times 10^{-3}$	$1.16 \times 10^{-4}$	$1.45 \times 10^{-4}$
HSO	$9.48 \times 10^{-4}$	$2.35 \times 10^{-6}$	$4.39 \times 10^{-6}$
SiOH	$8.58 \times 10^{-5}$	$1.99 \times 10^{-4}$	$6.35 \times 10^{-5}$
<i>cis</i> -HOCO	$7.38 \times 10^{-5}$	$1.36 \times 10^{-6}$	$1.22 \times 10^{-6}$
HOOO	$2.02 \times 10^{-2}$	$2.18 \times 10^{-7}$	$2.18 \times 10^{-3}$
<i>trans</i> -HOCO	$6.50 \times 10^{-5}$	$2.75 \times 10^{-7}$	$2.33 \times 10^{-7}$
HOSO	$2.07 \times 10^{-3}$	$1.81 \times 10^{-3}$	$1.81 \times 10^{-3}$
CH <sub>2</sub> Cl	$1.51 \times 10^{-8}$	$9.25 \times 10^{-9}$	$6.94 \times 10^{-9}$
FCO <sub>2</sub>	$1.96 \times 10^{-4}$	$2.30 \times 10^{-5}$	$3.64 \times 10^{-5}$

# The “Lego-brick” approach at work: data

## 1. The “parent\_molecule-radical TM”

**Table S2:** Comparison of experimental and computed ground-state rotational constants (MHz) at the B2PLYP/junTZ level and from the “parent\_molecule-radical TM” approach.

trans- $\beta$ -cyanovinyl radical						
	Experiment <sup>a</sup>	B2PLYP	Error (%)	TM	Error(%)	$\Delta B_{\text{vib}}^{\text{b}}$
$A_0$	65918.10(53)	67147.51	1.87	66011.01	0.14	-257.56
$B_0$	5067.06(59)	5063.43	0.07	5075.95	0.18	2.54
$C_0$	4685.71(57)	4700.35	0.31	4705.43	0.42	8.95
cis- $\beta$ -cyanovinyl radical						
	Experiment <sup>a</sup>	B2PLYP	Error (%)	TM	Error(%)	$\Delta B_{\text{vib}}^{\text{b}}$
$A_0$	49757.42(27)	50317.17	1.12	49601.36	0.31	-221.47
$B_0$	5364.31(16)	5373.28	0.17	5391.17	0.50	6.25
$C_0$	4832.54(13)	4845.28	0.26	4853.00	0.42	12.58
phenyl radical						
	Experiment <sup>c</sup>	B2PLYP	Error (%)	TM	Error(%)	$\Delta B_{\text{vib}}^{\text{b}}$
$A_0$	6280.203(113)	6323.48	1.37	6386.46	1.69	42.78
$B_0$	5599.597(92)	5643.50	1.52	5720.49	2.16	41.37
$C_0$	2959.40114(57)	2982.07	1.51	3018.56	2.00	22.04
trans- $\beta$ -chlorovinyl radical						
	Experiment <sup>d</sup>	B2PLYP	Error (%)	TM	Error(%)	$\Delta B_{\text{vib}}^{\text{b}}$
$A_0$	57457.5039(13)	58500.08	1.81	58064.53	1.06	-328.16
$B_0$	6483.86279(30)	6378.33	1.63	6457.15	0.41	47.03
$C_0$	5816.07623(31)	5741.33	1.29	5800.74	0.26	44.91
s-trans-CH <sub>2</sub> CHCO						
	Experiment <sup>e</sup>	B2PLYP	Error (%)	TM	Error(%)	$\Delta B_{\text{vib}}^{\text{b}}$
$A_0$	60392.2023(21)	61041.19	1.07	60571.02	0.30	543.20
$B_0$	4654.42551(55)	4644.55	0.21	4662.35	0.17	21.01
$C_0$	4322.76810(36)	4316.71	0.14	4329.71	0.16	20.29
linear CH <sub>2</sub> CHCO						
	Experiment <sup>e</sup>	B2PLYP	Error (%)	TM	Error(%)	$\Delta B_{\text{vib}}^{\text{b}}$
$A_0$	48845.53592(146)	49699.84	1.69	47854.37	2.03	459.47
$B_0$	4753.70918(38)	4726.00	0.58	4784.96	0.66	3.06
$C_0$	4327.29901(45)	4310.40	0.39	4345.31	0.42	11.00

<sup>a</sup> Taken from ref. S1. <sup>b</sup> Computed at the revDSD/junTZ level of theory. <sup>c</sup> Taken from ref. S2. <sup>d</sup> Taken from ref. S3. <sup>e</sup> <sup>35</sup>Cl isotopologue. <sup>e</sup> Taken from ref. S4

## 2. The $C_nS$ system

**Table S3: revDSD/junTZ structures<sup>a</sup> and corresponding rotational constants (MHz) for the  $C_nS$  species, with  $n = 2-6, 8,$  and  $10$ .**

Parameter	$C_2S$	$C_3S$	$C_4S$	$C_5S$	$C_6S$	$C_8S$	$C_{10}S$
$r(C1S)$	1.5568	1.54571	1.5618	1.5537	1.5612	1.5615	1.5625
$r(C1C2)$	1.3130	1.29677	1.2793	1.2858	1.2799	1.2800	1.2795
$r(C2C3)$		1.28285	1.2908	1.2688	1.2806	1.2786	1.2779
$r(C3C4)$			1.2955	1.2971	1.2734	1.2761	1.2772
$r(C4C5)$				1.2854	1.2938	1.2824	1.2796
$r(C5C6)$					1.2881	1.2699	1.2731
$r(C6C7)$						1.2960	1.2841
$r(C7C8)$						1.2836	1.2670
$r(C8C9)$							1.2973
$r(C9C10)$							1.2808
$B_e$	6464.54	2866.63	1515.56	915.87	595.92	297.09	170.12
$B_0(\text{revDSD})^b$	6459.07	2867.95	1515.91	916.87	596.37	297.60	174.72
diff% <sup>c</sup>	0.29%	0.77%	0.22%	0.67%	0.13%	0.07%	
$B_0(\text{exp})^d$	6477.75023(15)	2890.37959(29)	1519.2062(3)	922.7033(2)	597.12449(7)	297.81(1)	-

<sup>a</sup> Bond in Å, angles fixed to  $180^\circ$ . <sup>b</sup> Vibrational corrections to the rotational constants computed at the fc-CCSD(T)/cc-pVTZ level for  $C_2S$ ,  $C_3S$ , and  $C_4S$ . The fc-MP2/cc-pVTZ level is employed for  $C_5S$ , while for large species ( $C_6S$ ,  $C_8S$ , and  $C_{10}$ ) the fc-MP2/cc-pVDZ level was used. <sup>c</sup> Relative difference of  $B_0(\text{revDSD})$  with respect to experiment. <sup>d</sup> Experimental values taken from refs. S5–S7.

**Table S4: Semi-experimental equilibrium structure<sup>a</sup> of  $C_3S$  and  $C_5S$ .**

Parameter	$C_5S^b$	$C_3S^c$
$r(C1S)$	1.545(1)	1.5374(1)
$r(C1C2)$	1.278(2)	1.2927(1)
$r(C2C3)$	1.267(2)	1.281(7)
$r(C3C4)$	1.293(1)	
$r(C4C5)$	1.2795(6)	

<sup>a</sup> Bond distances in Å, angles fixed at  $180^\circ$ . <sup>b</sup> This work:  $r_e(\text{SE})$  obtained using the experimental ground-state rotational constants from ref. S6 and vibrational corrections at the MP2/cc-pVDZ level. Standard deviation of the LSQ fit:  $9 \times 10^{-5} u \cdot a_0$ . <sup>c</sup> From ref. S8.

**Table S5: TM+LR rotational constants (in MHz) for the  $C_nS$  species with  $n = 4, 6, 8,$  and  $10$ .<sup>a</sup>**

Parameter	$C_4S$	$C_6S$	$C_8S$	$C_{10}S$
$B_e(\text{TM+LR})$	1519.82	597.49	297.86	170.55
$B_0(\text{TM+LR})^b$	1520.16 (0.06%)	597.94 (0.14%)	298.37 (0.19%)	175.16
$B_0(\text{exp})^c$	1519.2062(3)	597.12499(7)	297.81(1)	-

<sup>a</sup> Angles have been kept fix at  $180^\circ$ . <sup>b</sup> Computed vibrational corrections to rotational constants are: at the fc-CCSD(T)/cc-pVTZ level for the  $C_4S$  species, and at the fc-MP2/cc-pVDZ level for longer chain ( $C_6S$ ,  $C_8S$ , and  $C_{10}$ ). <sup>c</sup> Experimental values taken from ref.<sup>S6</sup>

**Table S6: TM+LR rotational constants (in MHz) for linear and s-trans- $\text{CH}_2\text{CHO}$  species**

Parameter	linear $\text{CH}_2\text{CHcO}$	s-trans- $\text{CH}_2\text{CHcO}$
$A_e(\text{TM+LR})$	49469.38	61107.81
$B_e(\text{TM+LR})$	4769.80	4682.30
$C_e(\text{TM+LR})$	4350.31	4349.03
$A_0(\text{TM+LR})^a$	49009.92 (0.34%)	60558.62 (0.28%)
$B_0(\text{TM+LR})^a$	4766.73 (0.27%)	4661.29 (0.15%)
$C_0(\text{TM+LR})^a$	4339.34 (0.28%)	4328.74 (0.14%)
$A_0(\text{exp})^b$	48845.53592(146)	60392.2030(21)
$B_0(\text{exp})^b$	4753.70918(38)	4654.42551(55)
$C_0(\text{exp})^b$	4327.29901(45)	4322.76810(36)

<sup>a</sup> Computed vibrational corrections to rotational constants are at the revDSD/junTZ level of theory. <sup>b</sup> Experimental values taken from ref.<sup>S4</sup>

### 3. The 1- and 2-naphtalenyl radicals

Table S7: 1-naphtalenyl radical: revDSD/junTZ, TM (b), and TM (b+a) structures.<sup>a</sup>

Zmatrix of the 1-naphtalenyl radical							Parameter	revDSD	TM (b)	TM (b+a)
C							R1	1.3304	1.3345	1.3345
C	1	R1					R2	1.0842	1.0821	1.0821
H	2	R2	1	A1			R3	1.4020	1.4060	1.4060
C	1	R3	2	A2	3	D180	R4	1.0825	1.0804	1.0804
H	4	R4	1	A3	2	D180	R5	1.3562	1.3589	1.3589
C	4	R5	1	A4	2	D0	R6	1.0856	1.0831	1.0831
H	6	R6	4	A5	1	D180	R7	1.4211	1.4257	1.4257
C	6	R7	4	A6	1	D0	R8	1.4303	1.4330	1.4330
C	2	R8	1	A7	4	D0	R9	1.4198	1.4174	1.4174
C	9	R9	2	A8	1	D180	R10	1.4212	1.4189	1.4189
C	8	R10	6	A9	4	D180	R11	1.3537	1.3514	1.3514
C	11	R11	8	A10	6	D180	R12	1.3545	1.3522	1.3522
C	10	R12	9	A11	2	D180	R13	1.0845	1.0822	1.0822
H	10	R13	9	A12	2	D0	R14	1.0848	1.0810	1.0810
H	11	R14	8	A13	6	D0	R15	1.0839	1.0801	1.0801
H	13	R15	10	A14	9	D180	R16	1.0835	1.0797	1.0797
H	12	R16	11	A15	8	D180	A1	123.18	123.18	123.68
							A2	126.71	126.71	126.44
							A3	121.74	121.74	122.24
							A4	116.54	116.54	116.76
							A5	120.23	120.23	121.03
							A6	121.06	121.06	120.94
							A7	116.88	116.88	117.11
							A8	121.76	121.76	121.70
							A9	121.31	121.31	121.44
							A10	120.75	120.75	120.75
							A11	120.50	120.50	120.50
							A12	118.80	118.80	118.80
							A13	118.64	118.64	118.64
							A14	120.33	120.33	120.33
							A15	120.09	120.09	120.09
							D180	180.00	180.00	180.00
							D0	0.00	0.00	0.00

<sup>a</sup> For their definition, see main manuscript.

Table S8: 2-naphthalenyl radical: revDSD/junTZ, TM (b), and TM (b+a) structures.<sup>a</sup>

Zmatrix of the 2-naphthalenyl							Parameter	revDSD	TM (b)	TM (b+a)
C							R1	1.3306	1.3347	1.3347
C	1	R1					R2	1.0832	1.0811	1.0811
H	1	R2	2	A1			R3	1.4320	1.4347	1.4347
C	1	R3	2	A2	3	D180	R4	1.0844	1.0819	1.0819
H	4	R4	1	A3	2	D180	R5	1.3511	1.3557	1.3557
C	4	R5	1	A4	2	D0	R6	1.0843	1.0820	1.0820
H	6	R6	4	A5	1	D180	R7	1.4220	1.4267	1.4267
C	6	R7	4	A6	1	D0	R8	1.4025	1.4066	1.4066
C	2	R8	1	A7	4	D0	R9	1.4197	1.4174	1.4174
C	9	R9	2	A8	1	D180	R10	1.4209	1.4186	1.4186
C	8	R10	6	A9	4	D180	R11	1.3540	1.3516	1.3516
C	11	R11	8	A10	6	D180	R12	1.3533	1.3509	1.3509
C	10	R12	9	A11	2	D180	R13	1.0832	1.0794	1.0794
H	10	R13	9	A12	2	D0	R14	1.0847	1.0810	1.0810
H	11	R14	8	A13	6	D0	R15	1.0837	1.0800	1.0800
H	13	R15	10	A14	9	D180	R16	1.0835	1.0798	1.0798
H	12	R16	11	A15	8	D180	A1	122.84	122.84	123.34
							A2	116.57	116.57	116.80
							A3	118.94	118.94	119.74
							A4	120.60	120.60	120.47
							A5	120.34	120.34	120.30
							A6	121.14	121.14	121.21
							A7	126.73	126.73	126.46
							A8	124.50	124.50	124.62
							A9	122.23	122.23	122.01
							A10	120.65	120.65	120.65
							A11	120.03	120.03	120.03
							A12	118.75	118.75	118.75
							A13	118.68	118.68	118.68
							A14	120.10	120.10	120.10
							A15	120.18	120.18	120.18
							D180	180.00	180.00	180.00
							D0	0.00	0.00	0.00

<sup>a</sup> For their definition, see main manuscript.

## References

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