Hydrogen bonded networks in formamide $[HCONH_2]_n$ (n = 1 – 10) clusters: A computational exploration of preferred aggregation patterns

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Figure S8: AIM analysis on B3LYP/D95** optimized geometries of stacked (n = 2-10) formamide clusters. Line joining atoms indicate bond path as calculated using AIM2000.

Table S1: Comparison of Interaction energy (I.E) in kcal/mol in four arrangements of formamide n=1-10 at B3LYP/D95** level of theory. n = #monomers.

n	Linear				Circular				Helical				Stacked			
	a	b	c	d	a	b	c	d	a	b	c	d	a	b	c	d
2	-7.38	-5.88	-6.07	-5.41	-16.00	-14.0	-14.2	-12.70	-7.35	-6.36	-6.59	-5.79	-16.0	-14.0	-14.2	-12.7
3	-16.46	-13.44	-13.74	-12.38	-26.50	-26.5	-22.70	-20.40	-16.58	-14.45	-14.46	-13.20	-23.0	-19.9	-20.5	-18.1
4	-26.16	-21.80	-22.18	-20.08	-38.20	-32.4	-33.50	-29.70	-26.60	-22.77	-23.40	-20.62	-43.6	-36.9	-37.8	-33.7
5	-36.08	-30.13	-30.49	-27.76	-48.37	-42.75	-43.83	-39.12	-43.2	-36.2	-37.0	-33.0	-51.0	-43.3	-44.5	-39.6
6	-46.24	-39.35	-39.77	-36.25	-60.71	-54.02	-55.17	-49.44	-51.2	-43.8	-44.5	-40.2	-72.0	-60.8	-62.2	-55.7
7	-56.41	-48.26	-48.65	-44.44	-71.60	-63.73	-64.77	-58.47	-61.2	-52.5	-53.1	-48.2	-80.0	-72.3	-68.9	-61.1
8	-66.67	-57.62	-57.94	-53.03	-82.35	-73.17	-74.30	-67.04	-71.4	-61.1	-61.8	-56.1	-100.7	-84.8	-87.1	-77.8
9	-76.88	-66.68	-67.05	-61.39	-92.88	-82.35	-83.37	-75.52	-80.8	-67.4	-68.6	-62.0	-108.3	-91.3	-93.9	-83.7
10	-87.25	-75.52	-75.95	-69.54	-103.33	-91.48	-92.61	-83.84	-91.9	-79.5	-80.2	-73.1	-129.3	-108.9	-111.5	-99.9

a- BSSE uncorrected I.E for all arrangements optimized at B3LYP/D95** level;

b- BSSE corrected I.E for all arrangements at B3LYP/D95** level;

c- BSSE uncorrected I.E for all arrangements from single point calculations at B3LYP/cc-pVTZ level of theory;

d- BSSE corrected I.E for all arrangements from single point calculations at B3LYP/cc-pVTZ level of theory.

Table S2: O---H bond length (in Å) for formamide clusters n = (2-10)

Type	N	O---H bond length (in Å)															
		1	2	3	4	5	6	7	8	9	10						A
Linear	2	1.921															1.921
	3	1.873	1.878														1.876
	4	1.860	1.830	1.869													1.853
	5	1.853	1.815	1.816	1.861												1.836
	6	1.851	1.810	1.803	1.813	1.861											1.828
	7	1.849	1.810	1.796	1.797	1.809	1.858										1.820
	8	1.860	1.807	1.793	1.790	1.793	1.808	1.859									1.816
	9	1.863	1.809	1.793	1.989	1.789	1.795	1.810	1.863								1.814
	10	1.848	1.806	1.789	1.786	1.783	1.785	1.792	1.800	1.858							1.805
Circular	2	1.817	1.817														1.817
	3	1.807	1.804	1.807													1.806
	4	1.713	1.913	2.019	1.864	1.953											1.892
	5	1.750	1.797	1.696	1.649	1.667											1.712
	6	1.665	1.664	1.662	1.664	1.668	1.666										1.665
	7	1.624	1.671	1.662	1.612	1.644	1.776	1.667									1.665
	8	1.766	1.767	1.766	1.760	1.779	1.770	1.767	1.767								1.768
	9	1.769	1.768	1.769	1.777	1.761	1.766	1.767	1.766	1.772							1.768
	10	1.766	1.766	1.766	1.768	1.777	1.763	1.769	1.776	1.761	1.766						1.768
Helical	2	1.910															1.910
	3	1.879	1.884														1.882
	4	1.633	1.797	1.799													1.743
	5	1.768	1.890	1.943	1.890	1.879											1.874
	6	1.757	1.927	1.869	1.808	1.821	1.864										1.841
	7	1.757	1.928	1.869	1.803	1.807	1.814	1.863									1.834
	8	1.757	1.928	1.867	1.801	1.801	1.800	1.805	1.861								1.828
	9	1.762	1.923	1.872	1.810	1.788	1.783	1.785	1.797	1.855							1.819
	10	1.757	1.928	1.866	1.801	1.796	1.789	1.789	1.793	1.808	1.859						1.919
Stacked	2	1.817	1.817														1.817
	3	1.780	1.883	1.920													1.861
	4	1.762	1.951	1.950	1.950	1.951	1.764										1.888
	5	1.763	1.952	1.917	1.832	1.98	1.900	1.903									1.892
	6	1.757	1,960	1.920	1.931	1.915	1.915	1.931	1.920	1.960	1.757						1.897
	7	1.756	1.961	1.914	1.926	1.946	1.904	1.934	1.923	1.911	1.889	1.091					1.832
	8	1.757	1.962	1.929	1.916	1.909	1.926	1.899	1.899	1.926	1.909	1.916	1.929	1.962	1.757		1.900
	9	1.757	1.959	1.911	1.925	1.925	1.913	1.928	1.826	1.935	1.913	1.947	1.911	1.833	11.875	1.901	1.851
	10	1.756	1.961	1.916	1.927	1.912	1.930	1.895	1.896	1.923	1.923	1.896	1.895	1.930	1.912	-	1.905

Table S3: N-H bond stretching frequency (in cm^{-1}) for four arrangements of formamide clusters n = (1-10). ν indicates N-H stretching frequency, Ave ν indicates average N-H stretching frequency in a cluster and Δν indicates deviation of average N-H stretching frequency in a cluster from the ν value of the monomer.

	ν	n = 1	n = 2	n = 3	n = 4	n = 5	n = 6	n = 7	n = 8	n = 9	n = 10		ν	n = 1	n = 2	n = 3	n = 4	n = 5	n = 6	n = 7	n = 8	n = 9	n = 10
linear	ν_1	3606	3550	3508	3455	3440	3392	3371	3356	3354	3336	**helical**	ν_1	3606	3489	3415	3351	3115	3155	3155	3155	3169	3154
	ν_2		3604	3522	3495	3461	3415	3395	3378	3374	3354		ν_2		3604	3467	3372	3405	3362	3364	3363	3378	3348
	ν_3			3604	3505	3505	3430	3415	3393	3387	3370		ν_3			3603	3505	3476	3423	3401	3380	3420	3364
	ν_4				3603	3505	3492	3431	3411	3396	3380		ν_4				3603	3522	3463	3435	3405	3434	3369
	ν_5					3602	3496	3494	3418	3406	3384		ν_5					3547	3490	3461	3458	3446	3384
	ν_6						3603	3502	3470	3420	3406		ν_6					3603	3502	3492	3459	3454	3390
	ν_7							3603	3489	3460	3415		ν_7						3603	3494	3491	3463	3420
	ν_8								3603	3485	3489		ν_8							3603	3497	3500	3451
	ν_9									3603	3493		ν_9								3603	3544	3490
	ν_{10}										3603		ν_{10}									3603	3491
													ν_{11}										3603
	Ave ν	**3606**	**3577**	**3545**	**3515**	**3503**	**3471**	**3459**	**3440**	**3432**	**3423**		**Ave ν**	**3606**	**3546**	**3495**	**3458**	**3445**	**3428**	**3425**	**3423**	**3441**	**3406**
	Δν		**29**	**61**	**91**	**103**	**134**	**147**	**166**	**174**	**182**		**Δν**		**59**	**111**	**148**	**161**	**178**	**181**	**183**	**165**	**200**
circular	ν_1	3606	3239	3347	3337	3240	3220	3229	3228	3237	3239	**stack**	ν_1	3606	3239	3208	3143	3146	3131	3129	3130	3131	3128
	ν_2		3299	3386	3381	3262	3250	3251	3246	3252	3254		ν_2		3299	3364	3150	3262	3132	3311	3130	3249	3128
	ν_3			3388	3498	3285	3251	3260	3254	3258	3255		ν_3			3471	3413	3377	3329	3332	3329	3331	3330
	ν_4				3552	3310	3279	3279	3273	3279	3272		ν_4				3419	3420	3374	3377	3332	3334	3330
	ν_5					3326	3280	3286	3283	3282	3285		ν_5				3576	3460	3420	3391	3375	3373	3334
	ν_6						3289	3293	3292	3297	3291		ν_6				3597	3541	3421	3422	3381	3380	3374
	ν_7							3339	3297	3297	3297		ν_7					3601	3548	3526	3423	3386	3379
	ν_8								3326	3331	3304		ν_8						3548	3528	3523	3422	3382
	ν_9									3357	3337		ν_9						3575	3543	3541	3460	3421
	ν_{10}										3338		ν_{10}						3578	3559	3546	3515	3421
													ν_{11}							3578	3552	3521	3517
													ν_{12}								3575	3541	3521
													ν_{13}								3576	3551	3539
													ν_{14}									3570	3543
													ν_{15}									3578	3548
													ν_{16}										3551
													ν_{17}										3574
													ν_{18}										3575
	Ave ν	**3606**	**3269**	**3374**	**3442**	**3285**	**3262**	**3276**	**3275**	**3288**	**3278**		**Ave ν**	**3606**	**3269**	**3348**	**3383**	**3401**	**3406**	**3427**	**3416**	**3423**	**3422**
	Δν		**337**	**232**	**164**	**321**	**344**	**329**	**331**	**318**	**318**		**Δν**		**337**	**258**	**223**	**205**	**200**	**179**	**190**	**183**	**184**

Table S4: Average ρ value (in au) at bond critical point (BCP) of each cluster based on AIM aanlysis performed on optimized geometries obtained at B3LYP/D95** level for formamide clusters n = (2-10).

n	Linear		Circular		Helical		Stacked	
	ρ	Δ^2 ρ	ρ	Δ^2 ρ	ρ	Δ^2 ρ	ρ	Δ^2 ρ
2	0.023	0.022	0.035	0.026	0.025	0.021	0.035	0.026
3	0.023	0.025	0.032	0.028	0.028	0.024	0.031	0.024
4	0.028	0.026	0.030	0.024	0.030	0.025	0.030	0.024
5	0.029	0.027	0.037	0.028	0.027	0.023	0.029	0.023
6	0.030	0.027	0.038	0.030	0.031	0.026	0.029	0.023
7	0.031	0.028	0.038	0.030	0.031	0.026	0.027	0.022
8	0.031	0.028	0.038	0.030	0.031	0.027	0.028	0.023
9	0.032	0.028	0.038	0.030	0.031	0.028	0.028	0.023
10	0.032	0.028	0.038	0.030	0.032	0.027	0.030	0.022

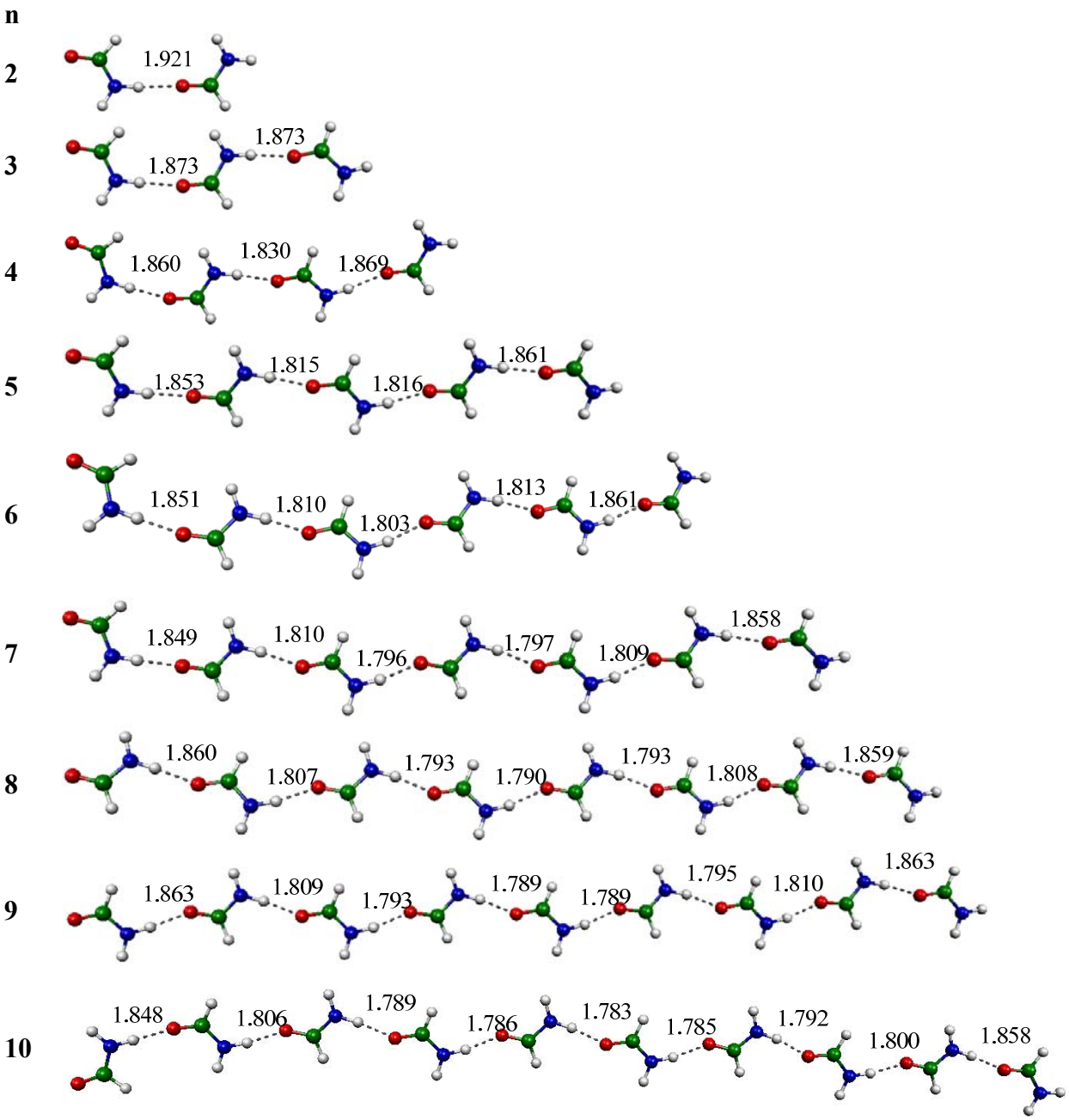

Figure S1: Optimized geometries of linear formamide clusters (n = 2 - 10) at B3LYP/D95** level of theory. O---H bond distances are in Å.

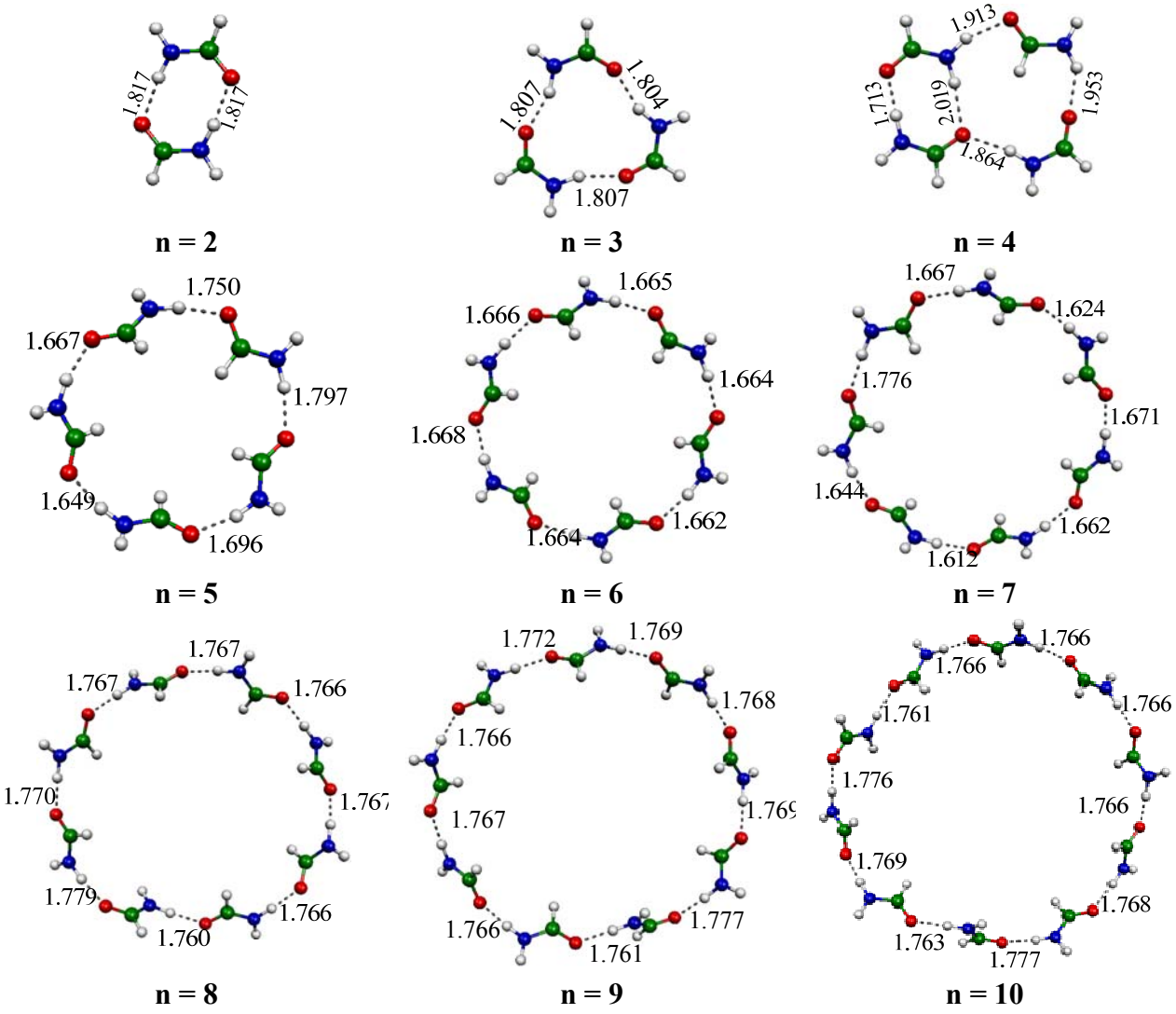

Figure S2: Optimized geometries of circular formamide clusters (n = 2 - 10) at B3LYP/D95** level of theory. O---H bond distances are in Å.

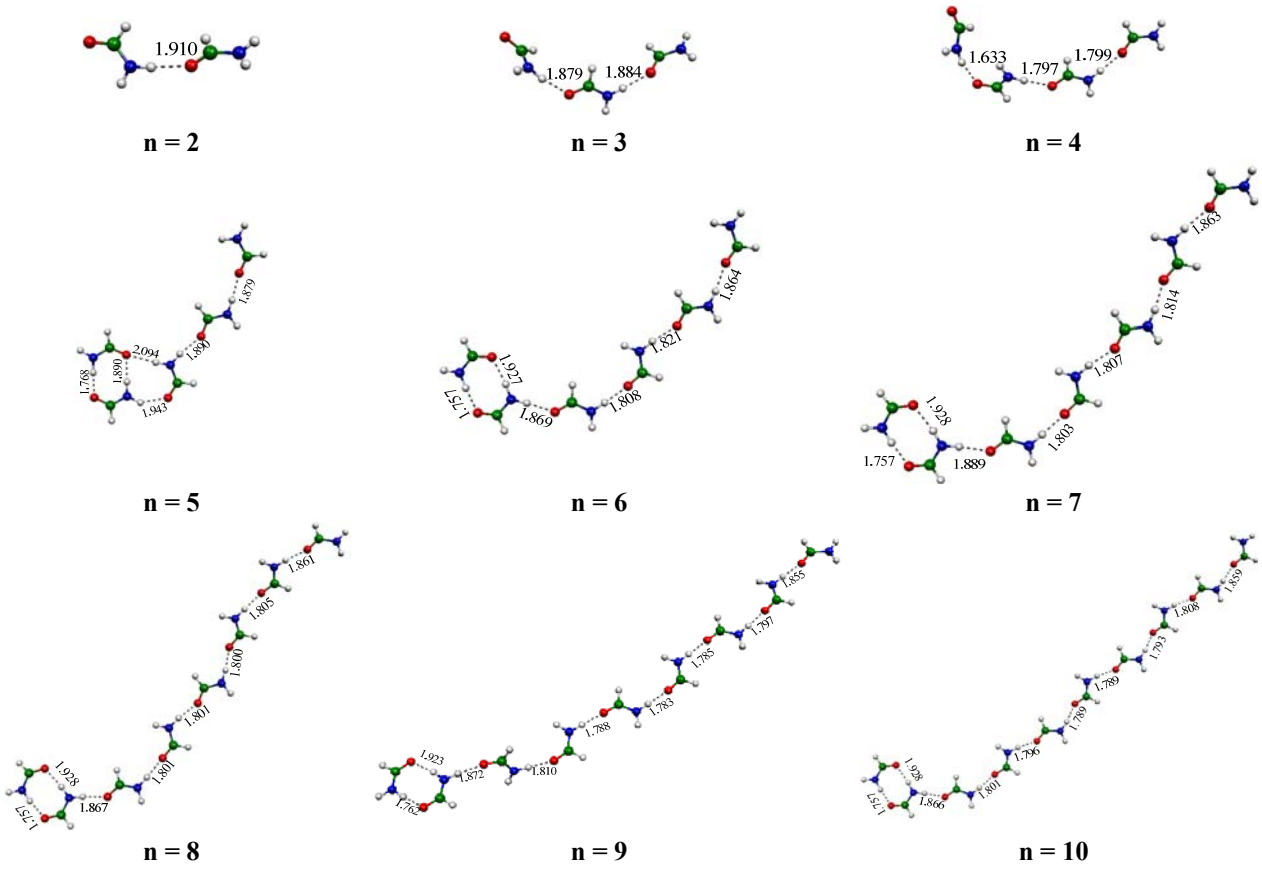

Figure S3: Optimized geometries of helical formamide clusters (n = 2 - 10) at B3LYP/D95** level of theory. O---H bond distances are in Å.

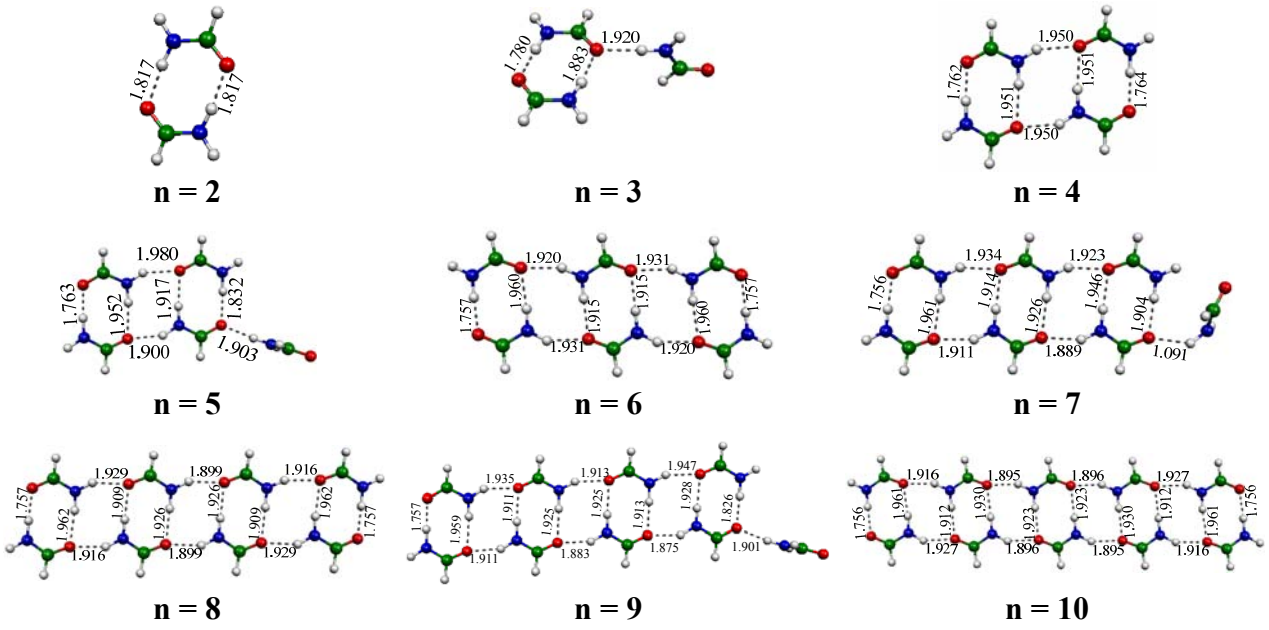

Figure S4: Optimized geometries of stacked formamide clusters (n = 2 - 10) at B3LYP/D95** level of theory. O---H bond distances are in Å.

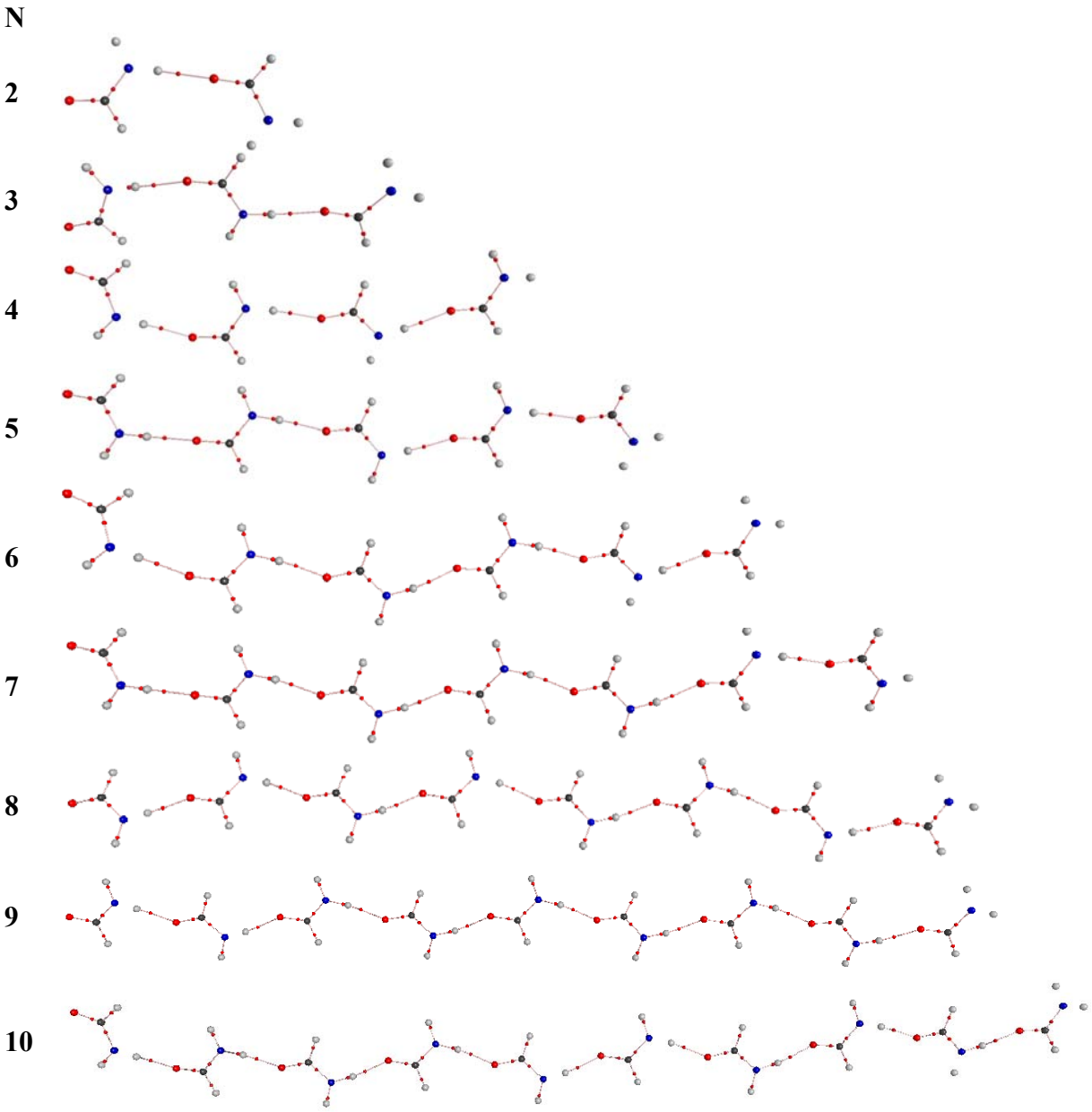

Figure S5: AIM analysis on B3LYP/D95** optimized geometries of linear (n = 2-10) formamide clusters. Line joining atoms indicate bond path as calculated using AIM2000.

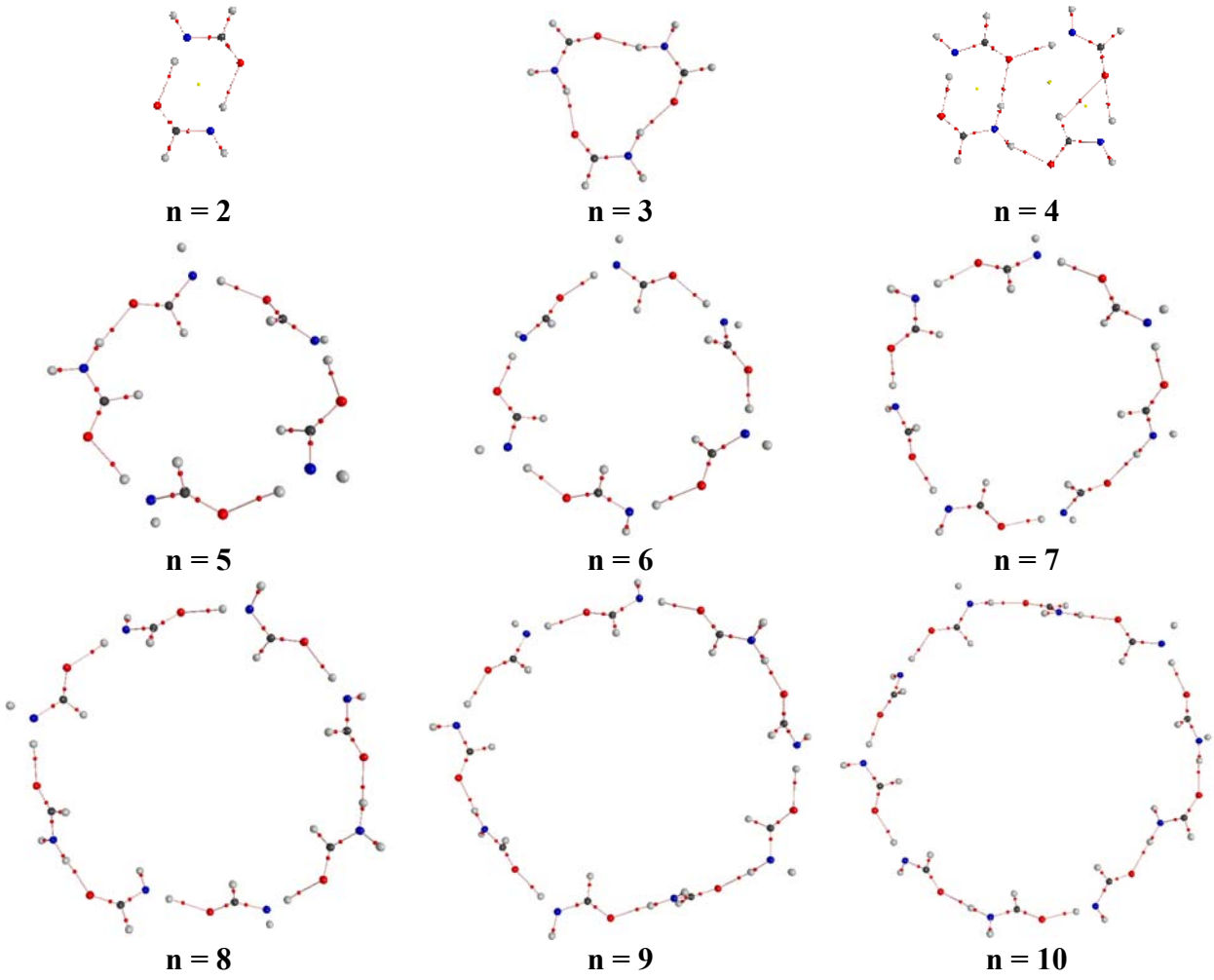

Figure S6: AIM analysis on B3LYP/D95** optimized geometries of circular (n = 2-10) formamide clusters. Line joining atoms indicate bond path as calculated using AIM2000.

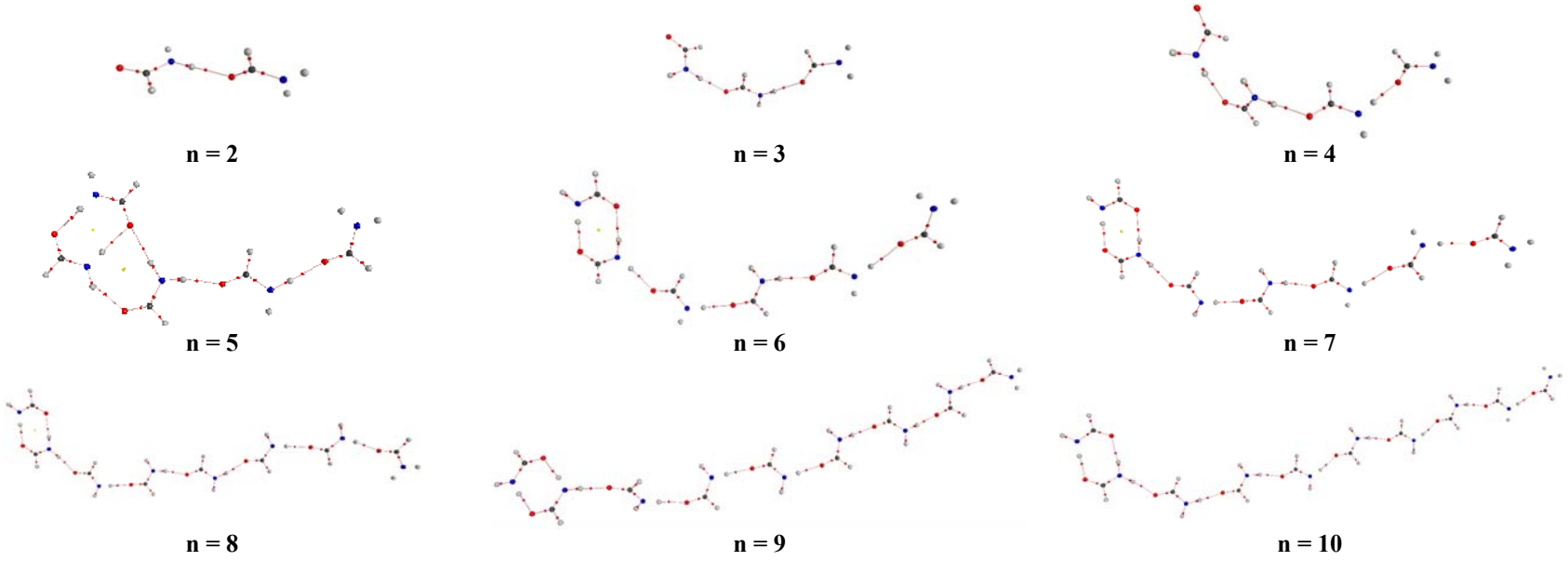

Figure S7: AIM analysis on B3LYP/D95** optimized geometries of helical (n = 2-10) formamide clusters. Line joining atoms indicate bond path as calculated using AIM2000.

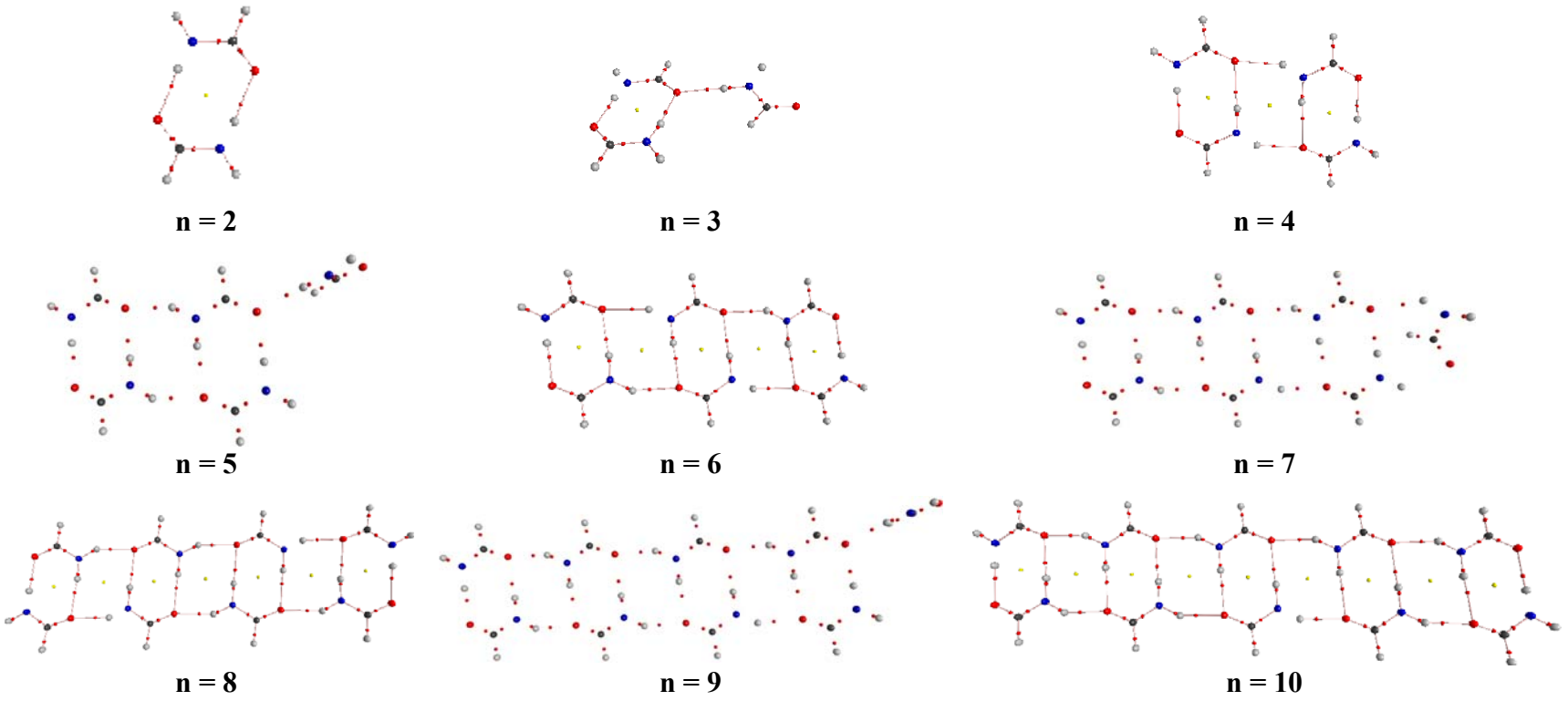

Figure S8: AIM analysis on B3LYP/D95** optimized geometries of stacked (n = 2-10) formamide clusters. Line joining atoms indicate bond path as calculated using AIM2000.