Supplementary Material for PCCP

Electronic Supplementary Information

The nature and strength of C−H···O interactions involving formyl hydrogen atoms: Computational and experimental studies of small aldehydes.

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Table S1. Optimized geometries and ESPD and NPA derived atomic charges for monomer and dimers.

Formaldehyde	Atom	x	y	z	q_{ESP}	q_{NPA}
	C	0.000000	0.000000	0.000000	0.43956	0.30990
	O	0.000000	0.000000	1.193934	-0.42852	-0.50689
	H	0.937978	0.000000	-0.579975	-0.00552	0.09850
	H	-0.937977	0.000000	-0.579978	-0.00552	0.09850
Ethylene						
	C	0.000000	0.000000	0.000000	-0.26199	-0.36677
	C	0.000000	0.000000	1.321964	-0.26199	-0.36677
	H	0.921387	0.000000	-0.566499	0.13099	0.18338
	H	-0.921387	0.000000	-0.566499	0.13099	0.18338
	H	-0.921387	0.000000	1.888463	0.13099	0.18338
	H	0.921387	0.000000	1.888463	0.13099	0.18338
Methanol						
	C	0.000000	0.000000	0.000000	0.24111	-0.19051
	H	0.000000	0.000000	1.086805	0.04238	0.17324
	H	1.036572	0.000000	-0.344524	-0.02613	0.15128
	H	-0.489335	-0.913802	-0.344524	-0.02613	0.15128
	O	-0.693970	1.158822	-0.411791	-0.61350	-0.74372
	H	-0.712098	1.189093	-1.368947	0.38228	0.45842
Acetaldehyde						
	C	0.000000	0.000000	0.000000	0.56773	0.45944
	O	0.000000	0.000000	1.197691	-0.49394	-0.53646
	H	0.957311	0.000000	-0.555894	-0.04404	0.09340
	C	-1.237893	0.000000	-0.846845	-0.30960	-0.68525
	H	-2.126132	0.000000	-0.222415	0.10823	0.22306
	H	-1.231160	-0.876790	-1.495989	0.08581	0.22290
	H	-1.231160	0.876790	-1.495989	0.08581	0.22290
Propionaldehyde						
	C	0.000000	0.000000	0.000000	0.45267	0.46574
	O	0.000000	0.000000	1.198328	-0.46489	-0.54213
	H	0.955799	0.000000	-0.558339	-0.03787	0.09806
	C	-1.241613	0.000000	-0.848425	0.06649	-0.49660
	H	-1.174583	0.869192	-1.509641	-0.00254	0.21807
	H	-1.174583	-0.869192	-1.509641	-0.00254	0.21807
	C	-2.524702	0.000000	-0.037002	-0.15276	-0.58295
	H	-2.570907	0.876529	0.605849	0.04923	0.20983
	H	-3.394631	0.000000	-0.689832	0.04297	0.20209
	H	-2.570907	-0.876529	0.605849	0.04923	0.20983
Trifluoroacetaldehyde						
	C	0.000000	0.000000	0.000000	0.37562	0.37141
	O	0.000000	0.000000	1.186494	-0.37875	-0.46276
	H	0.911207	0.000000	-0.619920	0.03000	0.13256

	C	-1.301684	0.000000	-0.820138	0.62532	1.01495
	F	-2.375028	0.000000	-0.059212	-0.19763	-0.34001
	F	-1.325757	1.077288	-1.605653	-0.22728	-0.35808
	F	-1.325763	-1.077293	-1.605646	-0.22728	-0.35808
Methyl formate						
	C	0.000000	0.000000	0.000000	0.69452	0.70497
	O	0.000000	0.000000	1.193636	-0.53144	-0.60148
	H	0.898404	0.000000	-0.626544	-0.02154	0.11433
	O	-1.084878	0.000000	-0.769428	-0.39751	-0.56482
	C	-2.328178	0.000000	-0.067487	0.06342	-0.20760
	H	-2.405754	-0.885428	0.559402	0.06360	0.18523
	H	-3.100115	0.000000	-0.828193	0.06535	0.18414
	H	-2.405754	0.885428	0.559402	0.06360	0.18523
N-Methylformamide						
	C	0.000000	0.000000	0.000000	0.52570	0.56766
	O	0.000000	0.000000	1.207540	-0.52067	-0.63383
	H	0.924065	0.000000	-0.598742	-0.01656	0.10536
	N	-1.120367	0.000000	-0.754214	-0.44495	-0.65827
	H	-1.031644	0.000000	-1.754329	0.27841	0.38826
	C	-2.430779	0.000000	-0.135636	-0.07169	-0.36797
	H	-2.555792	-0.880928	0.491786	0.08542	0.20204
	H	-3.189598	0.000000	-0.911899	0.07891	0.19473
	H	-2.555792	0.880928	0.491786	0.08542	0.20204
Acrolein						
	H	0.000000	0.000000	0.000000	-0.02342	0.09930
	C	0.000000	0.000000	1.107034	0.52708	0.41673
	O	1.027318	0.000000	1.727389	-0.48296	-0.52740
	C	-1.340050	0.000000	1.725337	-0.17981	-0.29337
	C	-2.427173	0.000000	0.964817	-0.28856	-0.29266
	H	-1.377850	0.000000	2.806982	0.13827	0.21187
	H	-3.423815	0.000000	1.382150	0.16791	0.19803
	H	-2.343810	0.000000	-0.115684	0.14148	0.18749
Benzaldehyde						
	C	0.000000	0.000000	0.000000	0.38709	0.44862
	O	0.000000	0.000000	1.200241	-0.44851	-0.53542
	H	0.950227	0.000000	-0.566464	0.00836	0.10422
	C	-1.222584	0.000000	-0.837654	0.04140	-0.17659
	C	-1.101244	0.000000	-2.221863	-0.19910	-0.16775
	H	-0.115623	0.000000	-2.671211	0.11384	0.20903
	C	-2.236778	0.000000	-3.019561	-0.03916	-0.20913
	H	-2.146129	0.000000	-4.096450	0.09168	0.21065
	C	-3.490770	0.000000	-2.425841	-0.08701	-0.17561
	H	-4.378188	0.000000	-3.043683	0.09552	0.20923
	C	-3.614979	0.000000	-1.039075	-0.08613	-0.20339
	H	-4.595841	0.000000	-0.585098	0.09771	0.21076

	C	-2.482865	0.000000	-0.244288	-0.08177	-0.15323
	H	-2.547879	0.000000	0.835168	0.10609	0.22862

Dimer Geometries

Formaldehyde	Atom	x	y	z	qESP	qNPA
A						
	C	0.000000	0.000000	0.000000	0.429661	0.31447
	O	0.000000	0.000000	1.197502	-0.425066	-0.53531
	H	0.945356	0.000000	-0.568366	-0.013397	0.09405
	H	-0.939639	0.000000	-0.570282	0.008803	0.12678
	H	-2.139617	0.000000	2.369270	0.008803	0.12678
	C	-3.079256	0.000000	1.798988	0.429661	0.31447
	O	-3.079256	0.000000	0.601486	-0.425066	-0.53531
	H	-4.024612	0.000000	2.367354	-0.013397	0.09405
B	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.419624	0.32555
	O	0.000000	0.000000	1.198524	-0.456488	-0.55917
	H	0.934646	0.000000	-0.581261	0.008106	0.10574
	H	-0.934550	-0.013429	-0.581261	0.008106	0.10574
	H	-0.029352	4.085453	0.902382	-0.009264	0.10500
	C	-0.021588	3.004735	0.690800	0.474632	0.31523
	O	-0.018647	2.595442	-0.434931	-0.442504	-0.52511
	H	-0.016639	2.315907	1.550088	-0.002213	0.12700
Acetaldehyde						
A	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.552730	0.45156
	O	0.000000	0.000000	1.202927	-0.488229	-0.56144
	H	0.956299	0.000000	-0.552088	-0.036443	0.12587
	C	-1.246751	0.000000	-0.832157	-0.293290	-0.68488
	H	-2.129822	0.000000	-0.200275	0.092916	0.22067
	H	-1.245063	0.875961	-1.482528	0.086160	0.22411
	H	-1.245040	-0.875942	-1.482553	0.086156	0.22411
	C	3.336041	-0.001299	0.949486	0.552733	0.45156
	O	3.336053	-0.001299	-0.253442	-0.488233	-0.56144
	H	2.379736	-0.000544	1.501564	-0.036442	0.12587
	C	4.582783	-0.002238	1.781655	-0.293293	-0.68488
	H	5.465859	-0.002957	1.149781	0.092916	0.22067
	H	4.581767	0.873743	2.431999	0.086161	0.22411
	H	4.580388	-0.878160	2.432076	0.086157	0.22411
B	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.565195	0.47726
	O	0.000000	0.000000	1.201935	-0.521201	-0.58047
	H	0.953901	0.000000	-0.555922	-0.036874	0.10089
	C	-1.236469	-0.029514	-0.844848	-0.281151	-0.68361

	H	-2.123910	0.050180	-0.223495	0.089371	0.21685
	H	-1.194609	0.788765	-1.562358	0.092564	0.23341
	H	-1.259680	-0.964276	-1.408080	0.070329	0.21963
	C	0.265970	3.039168	0.847839	0.556007	0.46265
	O	0.220848	2.688554	-0.301054	-0.487120	-0.56071
	H	0.256036	2.280785	1.650697	-0.018246	0.12520
	C	0.334367	4.471479	1.280357	-0.315731	-0.68374
	H	0.353752	5.133915	0.420312	0.101824	0.22138
	H	-0.526506	4.694625	1.912328	0.092919	0.22590
	H	1.223307	4.619114	1.895144	0.092114	0.22536
C	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.555935	0.46961
	O	0.000000	0.000000	1.200594	-0.508234	-0.55627
	H	0.962416	0.000000	-0.546811	-0.036859	0.09358
	C	-1.230210	0.000000	-0.851685	-0.343271	-0.69926
	H	-1.209372	-0.875360	-1.503418	0.089135	0.22233
	H	-2.132818	0.000000	-0.245982	0.154158	0.24768
	H	-1.209368	0.875361	-1.503420	0.089137	0.22233
	C	-4.183523	0.000226	2.208468	0.555934	0.46961
	O	-4.183536	0.000173	1.007875	-0.508235	-0.55627
	H	-5.145933	0.000349	2.755290	-0.036860	0.09358
	C	-2.953308	0.000150	3.060145	-0.343268	-0.69926
	H	-2.050702	0.000084	2.454438	0.154159	0.24768
	H	-2.974065	0.875541	3.711843	0.089136	0.22233
	H	-2.974226	-0.875180	3.711917	0.089133	0.22233
D	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.582748	0.47492
	O	0.000000	0.000000	1.201155	-0.524482	-0.57211
	H	0.955603	0.000000	-0.555404	-0.042555	0.09886
	C	-1.233402	0.000079	-0.847632	-0.297218	-0.68807
	H	-2.124020	-0.009357	-0.226044	0.094051	0.21796
	H	-1.217487	0.889424	-1.477987	0.103017	0.24160
	H	-1.220097	-0.870626	-1.504768	0.074449	0.21942
	C	0.315052	3.170966	0.697333	0.608785	0.47843
	O	0.155692	2.791664	-0.431444	-0.519455	-0.56653
	C	1.404405	2.699796	1.606329	-0.376332	-0.68819
	H	1.948342	3.560935	1.996645	0.090633	0.21997
	H	0.951183	2.180147	2.451975	0.126733	0.24372
	H	2.073285	2.021187	1.086040	0.126392	0.22235
	H	-0.378250	3.917312	1.127649	-0.046766	0.09767
E	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.585161	0.47815
	O	0.000000	0.000000	1.201193	-0.516567	-0.56961
	C	1.229970	0.000000	-0.850069	-0.347414	-0.68849
	H	-0.959133	-0.001959	-0.550650	-0.038708	0.09653

	H	2.122351	0.015046	-0.231315	0.111314	0.21961
	H	1.223174	-0.898249	-1.468294	0.117413	0.24405
	H	1.209126	0.864240	-1.515552	0.088800	0.21975
	C	0.844905	-2.893000	1.293885	0.585166	0.47815
	O	0.844898	-2.892976	0.092693	-0.516567	-0.56961
	C	-0.385056	-2.892957	2.143971	-0.347433	-0.68849
	H	-0.364241	-3.757211	2.809436	0.088804	0.21975
	H	-0.378210	-1.994719	2.762210	0.117419	0.24405
	H	-1.277443	-2.907949	1.525228	0.111319	0.21962
	H	1.804042	-2.891095	1.844523	-0.038710	0.09653
F	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.555071	0.44984
	O	0.000000	0.000000	1.202658	-0.502891	-0.56074
	H	0.955934	0.000000	-0.552827	-0.026296	0.12824
	C	-1.246947	-0.000966	-0.832087	-0.292911	-0.68467
	H	-2.130411	0.026484	-0.201183	0.095220	0.22016
	H	-1.232092	0.856913	-1.505532	0.084796	0.22341
	H	-1.256687	-0.894162	-1.458774	0.084440	0.22422
	C	3.977958	0.121109	0.207519	0.539905	0.47000
	O	3.332825	0.143811	-0.804832	-0.488091	-0.55792
	H	3.792095	-0.871942	2.067641	0.078972	0.22358
	C	3.401898	0.026248	1.585191	-0.288944	-0.69893
	H	3.753012	0.874587	2.175236	0.079786	0.22296
	H	2.314750	0.002710	1.565377	0.119221	0.24499
	H	5.082095	0.170685	0.153392	-0.038279	0.09487
G	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.556328	0.47188
	O	0.000000	0.000000	1.201572	-0.512173	-0.56652
	C	1.235719	0.000000	-0.843622	-0.265669	-0.69673
	H	1.193431	-0.817712	-1.563786	0.070359	0.22337
	H	1.256282	0.934970	-1.407484	0.095536	0.24639
	H	2.123071	-0.085453	-0.222345	0.084807	0.21715
	H	-0.956142	0.021375	-0.553134	-0.029189	0.10445
	C	0.339462	2.991557	0.805138	0.556328	0.47188
	O	0.123351	3.010768	-0.376684	-0.512173	-0.56652
	C	1.687391	2.761934	1.412640	-0.265668	-0.69673
	H	1.919007	3.562819	2.115503	0.070359	0.22337
	H	1.645179	1.828888	1.978480	0.095535	0.24639
	H	2.449570	2.700786	0.640613	0.084807	0.21715
	H	-0.490354	3.128907	1.521491	-0.029188	0.10445
Propionaldehyde						
A	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.500972	0.45700
	O	0.000000	0.000000	1.203144	-0.458233	-0.56523
	H	0.954260	0.000000	-0.556444	-0.065993	0.12887

	C	-1.249897	0.000000	-0.834372	-0.001898	-0.49625
	H	-1.188327	-0.868470	-1.496984	0.022242	0.21971
	H	-1.188327	0.868470	-1.496984	0.022242	0.21971
	C	-2.526637	0.000000	-0.013074	-0.174052	-0.58287
	H	-2.568134	0.876467	0.630373	0.049629	0.20870
	H	-3.401921	0.000000	-0.658819	0.055462	0.20167
	H	-2.568134	-0.876467	0.630373	0.049629	0.20870
	C	3.355424	0.000000	0.845110	0.500972	0.45700
	O	3.355424	0.000000	-0.358034	-0.458233	-0.56523
	H	2.401164	0.000000	1.401554	-0.065993	0.12887
	C	4.605321	0.000000	1.679482	-0.001898	-0.49625
	H	4.543750	0.868470	2.342094	0.022242	0.21971
	H	4.543750	-0.868470	2.342094	0.022242	0.21971
	C	5.882061	0.000000	0.858184	-0.174052	-0.58287
	H	6.757344	0.000000	1.503930	0.055462	0.20167
	H	5.923558	-0.876467	0.214737	0.049629	0.20870
	H	5.923558	0.876467	0.214737	0.049629	0.20870
B	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.430432	0.48433
	O	0.000000	0.000000	1.202007	-0.472585	-0.58333
	H	0.953243	0.000000	-0.557758	-0.027568	0.10512
	C	-1.241369	0.035137	-0.845903	0.072677	-0.49546
	H	-1.122456	-0.725810	-1.618798	0.000369	0.22753
	H	-1.239094	0.999241	-1.365164	-0.007662	0.21533
	C	-2.513477	-0.163716	-0.041691	-0.111030	-0.57995
	H	-3.390886	-0.110233	-0.682593	0.031104	0.20088
	H	-2.500840	-1.137377	0.445966	0.024634	0.20123
	H	-2.600589	0.591632	0.736254	0.032707	0.20873
	C	-0.014223	-3.044842	0.903725	0.503066	0.46640
	O	0.011225	-2.709546	-0.251029	-0.455577	-0.56508
	H	0.019734	-2.277836	1.697468	-0.044597	0.13045
	C	-0.097065	-4.473747	1.357737	-0.006763	-0.49615
	H	0.747495	-4.642326	2.032289	0.018761	0.22105
	H	-0.986058	-4.550169	1.991261	0.023948	0.22108
	C	-0.124436	-5.474760	0.216635	-0.152434	-0.58235
	H	-0.201132	-6.491047	0.596425	0.052166	0.20275
	H	-0.970147	-5.283241	-0.440535	0.044606	0.20879
	H	0.778935	-5.395118	-0.384589	0.043746	0.20866
C	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.440308	0.48193
	O	0.000000	0.000000	1.201618	-0.460964	-0.57316
	H	0.958029	0.000000	-0.553838	-0.021980	0.10180
	C	-1.232112	0.002696	-0.853891	0.039265	-0.50288
	H	-1.155959	0.884176	-1.496544	0.016834	0.24011
	H	-1.158524	-0.862222	-1.520536	0.004998	0.21660

	C	-2.522229	0.000008	-0.055568	-0.148165	-0.57926
	H	-3.384505	-0.040755	-0.717228	0.051412	0.20339
	H	-2.557387	-0.852216	0.620349	0.040976	0.20609
	H	-2.594186	0.903728	0.545922	0.037314	0.20537
	C	-0.673664	2.924155	1.237797	0.440316	0.48193
	O	-0.673596	2.924113	0.036180	-0.460965	-0.57315
	H	-1.631724	2.924233	1.791581	-0.021984	0.10180
	C	0.558398	2.921405	2.091759	0.039266	-0.50288
	H	0.482177	2.039911	2.734385	0.016836	0.24011
	H	0.484798	3.786308	2.758423	0.004995	0.21660
	C	1.848563	2.924068	1.293515	-0.148171	-0.57926
	H	1.883795	3.776309	0.617625	0.040973	0.20608
	H	2.710801	2.964780	1.955229	0.051416	0.20339
	H	1.920524	2.020361	0.692006	0.037319	0.20537
D	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.412332	0.48204
	O	0.000000	0.000000	1.201404	-0.447899	-0.57159
	H	0.960390	0.000000	-0.551229	-0.029409	0.09834
	C	-1.225825	-0.001958	-0.862610	0.102238	-0.49883
	H	-1.122893	0.847500	-1.543707	-0.005940	0.23338
	H	-1.160273	-0.895807	-1.491897	-0.015503	0.21675
	C	-2.528733	0.060994	-0.086690	-0.112209	-0.58877
	H	-3.378687	-0.055129	-0.755879	0.031165	0.20197
	H	-2.569065	-0.724366	0.666286	0.028422	0.20479
	H	-2.613124	1.022005	0.415809	0.036801	0.22192
	C	0.010989	3.023323	1.110096	0.412319	0.48205
	O	-0.821512	2.899930	0.252724	-0.447898	-0.57160
	H	1.042975	3.318545	0.837973	-0.029405	0.09834
	C	-0.221430	2.809247	2.575325	0.102254	-0.49883
	H	0.531195	2.086498	2.902830	-0.005942	0.23338
	H	0.037010	3.751066	3.070754	-0.015506	0.21675
	C	-1.625339	2.345354	2.918000	-0.112229	-0.58877
	H	-1.791985	1.347169	2.519224	0.036812	0.22192
	H	-1.765743	2.314765	3.996458	0.031161	0.20197
	H	-2.369483	3.014526	2.489227	0.028435	0.20479
Trifluoroacetaldehyde						
A	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.364692	0.37748
	O	0.000000	0.000000	1.189574	-0.376381	-0.49312
	H	0.914766	0.000000	-0.610243	0.036363	0.15532
	C	-1.309049	0.000000	-0.807389	0.629116	1.01512
	F	-2.376575	-0.000118	-0.036594	-0.206449	-0.34136
	F	-1.341825	1.077712	-1.591132	-0.223679	-0.35672
	F	-1.341718	-1.077580	-1.591316	-0.223661	-0.35672
	C	2.993076	0.000476	1.881803	0.364692	0.37748

	O	2.993076	0.000281	0.692230	-0.376381	-0.49312
	H	2.078310	0.000394	2.492047	0.036363	0.15532
	C	4.302125	0.000877	2.689192	0.629116	1.01512
	F	5.369651	0.000852	1.918397	-0.206449	-0.34136
	F	4.334680	1.078725	3.472758	-0.223679	-0.35672
	F	4.335015	-1.076568	3.473297	-0.223661	-0.35672
B	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.345658	0.38906
	O	0.000000	0.000000	1.189901	-0.382104	-0.50951
	H	0.906889	0.000000	-0.622284	0.059424	0.14305
	C	-1.320951	-0.064079	-0.790687	0.564526	1.01981
	F	-2.307260	0.526493	-0.133389	-0.188181	-0.35427
	F	-1.190565	0.503899	-1.981692	-0.200762	-0.35193
	F	-1.649251	-1.343433	-0.978848	-0.205072	-0.35533
	C	-0.605714	2.927671	0.837394	0.398944	0.37927
	O	-0.230513	2.625527	-0.251134	-0.401048	-0.48888
	H	-0.779407	2.199991	1.646273	0.014803	0.15745
	C	-0.881667	4.391427	1.217620	0.647372	1.01850
	F	-0.703623	5.211939	0.204135	-0.204839	-0.33941
	F	-2.134320	4.503077	1.654020	-0.224954	-0.35348
	F	-0.066963	4.744905	2.210673	-0.223766	-0.35431
C	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.365133	0.38331
	O	0.000000	0.000000	1.188806	-0.413749	-0.49409
	H	0.912985	0.000000	-0.614699	0.031654	0.14424
	C	-1.307197	-0.003513	-0.810394	0.671781	1.01607
	F	-2.371124	0.081862	-0.040605	-0.205920	-0.33973
	F	-1.300407	1.022970	-1.659491	-0.233670	-0.35546
	F	-1.376197	-1.126364	-1.524268	-0.231684	-0.35475
	C	2.621543	0.344986	3.004151	0.299787	0.36668
	O	3.353544	0.429596	3.935544	-0.373177	-0.46657
	H	1.539272	0.168182	3.066991	0.081403	0.15511
	C	3.147229	0.479616	1.561529	0.735574	1.01634
	F	4.443359	0.701763	1.519824	-0.234431	-0.33932
	F	2.883433	-0.639151	0.877844	-0.245714	-0.36665
	F	2.522587	1.484347	0.940333	-0.246990	-0.36516
Methyl formate						
A	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.634201	0.70322
	O	0.000000	0.000000	1.198250	-0.486016	-0.63081
	H	0.902562	0.000000	-0.616250	-0.011168	0.14588
	O	-1.094377	0.000000	-0.754593	-0.379744	-0.56235
	C	-2.330279	0.000000	-0.041484	0.090127	-0.20773
	H	-2.402052	-0.885272	0.586341	0.045893	0.18414
	H	-3.110098	0.000000	-0.794311	0.060815	0.18350

	H	-2.402053	0.885272	0.586341	0.045893	0.18414
	C	3.090118	0.000000	1.528192	0.634201	0.70322
	O	3.090118	0.000000	0.329942	-0.486016	-0.63081
	H	2.187556	0.000000	2.144441	-0.011168	0.14588
	O	4.184495	0.000000	2.282785	-0.379744	-0.56235
	C	5.420397	0.000000	1.569676	0.090127	-0.20773
	H	5.492170	-0.885272	0.941851	0.045893	0.18414
	H	6.200216	0.000000	2.322502	0.060815	0.18350
	H	5.492170	0.885272	0.941851	0.045893	0.18414
B	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.745082	0.71206
	O	0.000000	0.000000	1.197030	-0.620753	-0.62353
	H	0.903485	0.000000	-0.618748	-0.008188	0.11400
	O	-1.076394	0.000123	-0.770235	-0.482384	-0.55977
	C	-2.330449	0.000929	-0.077671	0.182250	-0.20603
	H	-2.415616	-0.874114	0.560024	0.069736	0.18931
	H	-3.096369	-0.010640	-0.843679	0.049008	0.18819
	H	-2.421571	0.890981	0.538839	0.065250	0.18578
	C	-4.293901	-0.131311	3.484522	0.745090	0.71206
	O	-4.293907	-0.131338	2.287493	-0.620755	-0.62353
	H	-5.197384	-0.131244	4.103274	-0.008197	0.11400
	O	-3.217505	-0.131475	4.254754	-0.482378	-0.55977
	C	-1.963452	-0.132335	3.562187	0.182228	-0.20603
	H	-1.872364	-1.022397	2.945683	0.065253	0.18578
	H	-1.197530	-0.120791	4.328194	0.049012	0.18819
	H	-1.878250	0.742702	2.924487	0.069745	0.18931
C	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.619528	0.69805
	O	0.000000	0.000000	1.193334	-0.498651	-0.59992
	H	0.889584	0.000000	-0.637301	-0.039473	0.13111
	O	-1.096780	0.000000	-0.762133	-0.298031	-0.57895
	C	-2.333342	0.000000	-0.046809	-0.022722	-0.20657
	H	-2.403240	-0.885325	0.580801	0.074758	0.18646
	H	-3.114958	0.000000	-0.797905	0.089834	0.18335
	H	-2.403256	0.885343	0.580773	0.074756	0.18646
	C	0.366823	0.000000	-3.799311	0.619528	0.69805
	O	0.366824	0.000000	-4.992646	-0.498651	-0.59992
	H	-0.522761	-0.000039	-3.162010	-0.039472	0.13111
	O	1.463605	0.000000	-3.037180	-0.298032	-0.57895
	C	2.700166	0.000000	-3.752504	-0.022719	-0.20656
	H	2.770071	-0.885335	-4.380099	0.074757	0.18646
	H	3.481782	0.000000	-3.001408	0.089834	0.18335
	H	2.770072	0.885333	-4.380101	0.074756	0.18646
N-Methylformamide						
A	Atom	x	y	z	qESP	qNPA

	C	0.000000	0.000000	0.000000	0.563113	0.55222
	O	0.000000	0.000000	1.215053	-0.502783	-0.66530
	H	0.924918	0.000000	-0.593568	-0.049721	0.14792
	N	-1.129112	0.000000	-0.737076	-0.472288	-0.65237
	H	-1.050255	0.000000	-1.738013	0.296928	0.39001
	C	-2.433015	0.000000	-0.105990	-0.061161	-0.36807
	H	-2.551275	-0.880737	0.523173	0.072120	0.20076
	H	-3.200251	-0.000131	-0.874008	0.081684	0.19408
	H	-2.551389	0.880860	0.522984	0.072108	0.20075
	C	3.225598	0.000563	0.811209	0.563109	0.55222
	O	3.225591	0.000491	-0.403844	-0.502778	-0.66530
	H	2.300683	0.000326	1.404783	-0.049720	0.14792
	N	4.354715	0.000938	1.548279	-0.472289	-0.65237
	H	4.275862	0.000978	2.549217	0.296928	0.39001
	C	5.658615	0.001273	0.917187	-0.061163	-0.36807
	H	5.777141	-0.879488	0.288108	0.072121	0.20076
	H	6.425853	0.001451	1.685202	0.081684	0.19408
	H	5.776713	0.882108	0.288128	0.072108	0.20075
B	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.692709	0.57063
	O	0.000000	0.000000	1.211299	-0.633363	-0.65712
	H	0.928563	0.000000	-0.591445	-0.038401	0.10442
	N	-1.111506	-0.003374	-0.758290	-0.706544	-0.64985
	H	-1.009011	0.017051	-1.757153	0.338957	0.38689
	C	-2.434303	-0.000173	-0.158706	0.179660	-0.37025
	H	-2.528101	-0.802839	0.567039	0.081027	0.21621
	H	-3.179946	-0.136548	-0.935438	0.028472	0.19833
	H	-2.631510	0.935630	0.361721	0.057505	0.20075
	C	-4.532128	-0.241007	3.326292	0.692700	0.57063
	O	-4.532150	-0.240372	2.114995	-0.633301	-0.65712
	H	-5.460681	-0.241372	3.917750	-0.038417	0.10442
	N	-3.420613	-0.237936	4.084576	-0.706722	-0.64985
	H	-3.523110	-0.259069	5.083425	0.338941	0.38688
	C	-2.097809	-0.240860	3.485005	0.180562	-0.37025
	H	-2.004229	0.561797	2.759229	0.080718	0.21623
	H	-1.352206	-0.104245	4.261732	0.028309	0.19833
	H	-1.900346	-1.176638	2.964623	0.057188	0.20073
C	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.508469	0.56227
	O	0.000000	0.000000	1.211417	-0.554661	-0.65220
	H	0.928955	0.000000	-0.593870	-0.029869	0.10188
	N	-1.103821	0.007031	-0.768636	-0.281227	-0.67910
	H	-0.983262	-0.019248	-1.773695	0.191273	0.42946
	C	-2.419635	-0.031291	-0.167681	-0.140838	-0.36714
	H	-2.584908	-0.974473	0.353169	0.083083	0.19529

	H	-3.167731	0.083987	-0.946316	0.087565	0.19371
	H	-2.525089	0.772727	0.558801	0.086130	0.20075
	C	0.355201	1.641855	-3.237715	0.551613	0.56630
	O	-0.108541	0.540774	-3.461776	-0.484833	-0.66573
	H	0.211129	2.155465	-2.275853	-0.042873	0.12086
	N	1.085784	2.336525	-4.122774	-0.463897	-0.64097
	H	1.423601	3.245655	-3.861019	0.300735	0.39425
	C	1.371678	1.802700	-5.441406	-0.045477	-0.36908
	H	1.815764	0.813630	-5.352190	0.076357	0.20883
	H	2.064245	2.466279	-5.948947	0.084700	0.19903
	H	0.458379	1.714249	-6.027477	0.073751	0.20158

Acrolein

A	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.498782	0.40729
	O	0.000000	0.000000	1.205437	-0.479528	-0.55267
	H	0.946727	0.000000	-0.569680	-0.010764	0.12883
	C	-1.227494	0.000000	-0.816413	-0.151427	-0.29556
	H	-2.171174	0.000000	-0.286258	0.120785	0.20980
	C	-1.141885	0.000000	-2.140972	-0.291505	-0.28653
	H	-2.016322	0.000000	-2.775899	0.162684	0.19605
	H	-0.174197	0.000000	-2.628699	0.150973	0.19278
	C	3.337749	0.000218	0.763635	0.498783	0.40729
	O	3.337756	0.000218	-0.441802	-0.479529	-0.55267
	H	2.391020	0.000106	1.333310	-0.010764	0.12883
	C	4.565241	0.000432	1.580054	-0.151427	-0.29556
	H	5.508922	0.000528	1.049905	0.120785	0.20980
	C	4.479624	0.000498	2.904612	-0.291505	-0.28653
	H	5.354057	0.000654	3.539544	0.162684	0.19605
	H	3.511933	0.000397	3.392334	0.150973	0.19278

B	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.507868	0.42659
	O	0.000000	0.000000	1.203919	-0.500380	-0.55259
	H	0.952947	0.000000	-0.562582	-0.008724	0.10088
	C	-1.215626	0.000000	-0.830755	-0.216956	-0.31070
	H	-2.172466	0.000000	-0.320547	0.189463	0.23887
	C	-1.102798	0.000000	-2.153680	-0.259642	-0.28556
	H	-1.966848	0.000000	-2.802491	0.163983	0.19913
	H	-0.127624	0.000000	-2.627138	0.124388	0.18338
	C	-4.194209	0.000000	2.026915	0.507868	0.42659
	O	-4.194209	0.000000	0.822996	-0.500380	-0.55259
	H	-5.147156	0.000000	2.589497	-0.008724	0.10088
	C	-2.978583	0.000000	2.857670	-0.216956	-0.31070
	H	-2.021742	0.000000	2.347461	0.189463	0.23887
	C	-3.091410	0.000000	4.180594	-0.259642	-0.28556
	H	-2.227360	0.000000	4.829406	0.163983	0.19913

	H	-4.066585	0.000000	4.654052	0.124388	0.18338
C	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.472823	0.40574
	O	0.000000	0.000000	1.205798	-0.486149	-0.55468
	H	0.947330	0.000000	-0.568134	0.010120	0.13348
	C	-1.227165	0.000000	-0.816095	-0.143913	-0.29599
	H	-2.171513	0.000000	-0.287121	0.122941	0.20942
	C	-1.138941	0.000000	-2.140611	-0.288130	-0.28627
	H	-2.012326	0.000000	-2.777249	0.158175	0.19548
	H	-0.169801	0.000000	-2.625730	0.151655	0.19415
	C	3.927981	0.000000	0.044590	0.489630	0.42580
	O	3.281362	0.000000	-0.970720	-0.479987	-0.55236
	H	5.033827	0.000000	0.007782	-0.012486	0.10149
	C	3.352058	0.000000	1.400338	-0.165535	-0.31104
	H	2.271239	0.000000	1.492767	0.156300	0.23557
	C	4.162668	0.000000	2.452106	-0.286407	-0.28371
	H	3.787333	0.000000	3.465435	0.167351	0.19916
	H	5.238953	0.000000	2.323008	0.133614	0.18375
D	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.584768	0.41331
	O	0.000000	0.000000	1.203060	-0.515403	-0.54408
	H	0.941532	0.000000	-0.577842	-0.068584	0.10768
	C	-1.216522	0.000000	-0.832021	-0.215221	-0.30204
	H	-2.167972	0.000000	-0.315572	0.134035	0.20747
	C	-1.104767	0.000000	-2.155570	-0.261930	-0.28968
	H	-1.970748	0.000000	-2.802717	0.150772	0.19158
	H	-0.125857	0.000000	-2.621081	0.161215	0.21048
	C	3.366943	0.000696	-1.994616	0.514127	0.42360
	O	2.355518	0.000226	-2.645817	-0.474455	-0.54947
	H	3.331248	0.001170	-0.888351	0.002509	0.10520
	C	4.721085	0.000691	-2.572907	-0.193350	-0.29829
	H	4.792039	0.000222	-3.652663	0.139859	0.21372
	C	5.783495	0.001251	-1.777794	-0.256241	-0.27944
	H	6.792305	0.001267	-2.164833	0.164627	0.19959
	H	5.667044	0.001716	-0.700544	0.133273	0.19037
E	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.523572	0.41834
	O	0.000000	0.000000	1.202226	-0.500343	-0.54047
	H	0.950847	0.000000	-0.567499	-0.023959	0.09714
	C	-1.216998	-0.001707	-0.828272	-0.190197	-0.30274
	H	-2.170036	0.001396	-0.317214	0.136978	0.21393
	C	-1.135263	-0.007929	-2.152916	-0.249903	-0.28455
	H	-2.021969	-0.012262	-2.770253	0.172691	0.21326
	H	-0.169997	-0.009492	-2.646592	0.117326	0.18139
	C	-5.322441	-0.544955	-1.136509	0.529458	0.42712

	O	-4.340945	-0.208654	-1.744061	-0.487930	-0.54959
	H	-6.230111	-0.887316	-1.667755	-0.020810	0.10365
	C	-5.426825	-0.540474	0.333137	-0.192658	-0.29889
	H	-4.557964	-0.210549	0.888275	0.148001	0.21420
	C	-6.550501	-0.929341	0.922115	-0.266034	-0.28130
	H	-6.664066	-0.939818	1.996555	0.165081	0.20051
	H	-7.399476	-1.253366	0.331678	0.138727	0.18799

Benzaldehyde

A	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.403599	
	O	0.000000	0.000000	1.205591	-0.440446	
	H	0.949831	0.000000	-0.561623	0.007527	
	C	-1.231692	-0.004082	-0.822889	-0.027037	
	C	-2.485674	0.004332	-0.216045	-0.023742	
	H	-2.538824	0.018372	0.864039	0.078985	
	C	-3.626580	-0.005326	-0.997553	-0.124861	
	H	-4.602831	0.002121	-0.533671	0.102303	
	C	-3.517404	-0.023953	-2.385668	-0.053006	
	H	-4.410976	-0.032281	-2.994641	0.084921	
	C	-2.269889	-0.031758	-2.993234	-0.072372	
	H	-2.191152	-0.046514	-4.070997	0.089337	
	C	-1.125191	-0.021102	-2.208930	-0.130905	
	H	-0.143685	-0.028099	-2.666854	0.105698	
	C	3.289591	-0.414402	0.996218	0.403600	
	O	3.309959	-0.210568	-0.191841	-0.440447	
	H	2.348912	-0.322792	1.565718	0.007525	
	C	4.482405	-0.799405	1.785645	-0.027038	
	C	4.351235	-1.029270	3.150452	-0.130905	
	H	3.379880	-0.920663	3.617114	0.105698	
	C	5.458123	-1.397012	3.902212	-0.072373	
	H	5.359824	-1.578022	4.963138	0.089337	
	C	6.692953	-1.531785	3.283728	-0.053006	
	H	7.557063	-1.818308	3.867343	0.084921	
	C	6.827096	-1.300542	1.917104	-0.124861	
	H	7.793488	-1.406674	1.444735	0.102303	
	C	5.723682	-0.934982	1.167867	-0.023742	
	H	5.796795	-0.749247	0.104965	0.078985	

B	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.378961	
	O	0.000000	0.000000	1.203052	-0.435326	
	H	0.954463	0.000000	-0.559061	0.008693	
	C	-1.213124	0.000000	-0.844580	-0.006736	
	C	-2.480987	0.000000	-0.266965	-0.021955	
	H	-2.588704	0.000000	0.807924	0.080845	
	C	-3.603027	0.000000	-1.076115	-0.069956	

	H	-4.584508	0.000000	-0.623491	0.095903	
	C	-3.461143	0.000000	-2.460683	-0.101685	
	H	-4.340032	0.000000	-3.091002	0.095789	
	C	-2.199122	0.000000	-3.039719	-0.041256	
	H	-2.094334	0.000000	-4.115303	0.084138	
	C	-1.073916	0.000000	-2.228666	-0.170085	
	H	-0.082719	0.000000	-2.665715	0.102671	
	C	-4.338504	0.000000	3.646736	0.378961	
	O	-4.338504	0.000000	2.443684	-0.435326	
	H	-5.292967	0.000000	4.205797	0.008693	
	C	-3.125380	0.000000	4.491317	-0.006736	
	C	-3.264587	0.000000	5.875402	-0.170085	
	H	-4.255785	0.000000	6.312451	0.102671	
	C	-2.139382	0.000000	6.686456	-0.041256	
	H	-2.244169	0.000000	7.762039	0.084138	
	C	-0.877361	0.000000	6.107419	-0.101685	
	H	0.001529	0.000000	6.737738	0.095789	
	C	-0.735476	0.000000	4.722851	-0.069956	
	H	0.246005	0.000000	4.270227	0.095903	
	C	-1.857517	0.000000	3.913701	-0.021955	
	H	-1.749800	0.000000	2.838812	0.080845	

C	Atom	x	y	z	qESP	qNPA
	C	0.000000	0.000000	0.000000	0.427881	0.44169
	O	0.000000	0.000000	1.202802	-0.475299	-0.54885
	H	0.943053	0.000000	-0.574090	-0.005877	0.12348
	C	-1.227224	0.000000	-0.832024	-0.020083	-0.17402
	C	-2.486449	0.000000	-0.236055	-0.064631	-0.15683
	H	-2.550003	0.000000	0.843570	0.097540	0.22615
	C	-3.619768	0.000000	-1.028772	-0.088456	-0.20820
	H	-4.600541	0.000000	-0.574311	0.088404	0.20788
	C	-3.496912	0.000000	-2.416133	-0.088336	-0.17989
	H	-4.385281	0.000000	-3.032884	0.090105	0.20606
	C	-2.243398	0.000000	-3.010761	-0.082458	-0.21052
	H	-2.154413	0.000000	-4.087985	0.096966	0.20723
	C	-1.104275	0.000000	-2.217255	-0.091923	-0.17166
	H	-0.116520	0.000000	-2.661137	0.070175	0.23182
	C	3.497834	0.000000	-2.718072	0.279713	0.46011
	O	2.296269	0.000000	-2.778776	-0.370166	-0.56030
	H	4.011290	0.000000	-1.739324	0.053090	0.11029
	C	4.392808	-0.000051	-3.895174	0.072682	-0.18050
	C	5.770005	-0.000073	-3.704426	-0.168629	-0.16311
	H	6.169284	-0.000053	-2.697640	0.098617	0.21079
	C	6.622139	-0.000120	-4.799141	-0.042648	-0.20827
	H	7.693126	-0.000138	-4.655083	0.095708	0.21231
	C	6.090854	-0.000145	-6.080847	-0.113083	-0.17097

H	6.752415	-0.000182	-6.936090	0.106128	0.21047
C	4.711773	-0.000123	-6.274301	-0.053590	-0.20295
H	4.308177	-0.000142	-7.276851	0.091636	0.21183
C	3.862227	-0.000075	-5.183406	-0.115044	-0.15106
H	2.787655	-0.000057	-5.303785	0.111579	0.22702

Table S2. Topological analysis of the electron density at bond critical points for the monomer.

Formaldehyde	Bond	ρ (a. u.)	$\nabla^2\rho$ (a. u.)	ε
	C1-O2	0.4320	-0.0183	0.0922
	C1-H3	0.2853	-1.0430	0.0129
	C1-H4	0.2853	-1.0430	0.0129
Ethylene	Bond	ρ (a. u.)	$\nabla^2\rho$ (a. u.)	ε
	C1-C2	0.3560	-1.1250	0.2951
	C1-H3	0.2885	-1.0570	0.0033
	C1-H4	0.2885	-1.0570	0.0033
Methanol	Bond	ρ (a. u.)	$\nabla^2\rho$ (a. u.)	ε
	C1-O5	0.2601	-0.4918	0.0013
	C1-H2	0.2910	-1.0700	0.0413
	C1-H3/H4	0.2864	-1.0300	0.0456
	O5-H6	0.3801	-2.9450	0.0214
Acetaldehyde	Bond	ρ (a. u.)	$\nabla^2\rho$ (a. u.)	ε
	C1-O2	0.4297	-0.0739	0.0876
	C1-H3	0.2827	-1.0200	0.0128
	C1-C4	0.2619	-0.6508	0.0494
	C4-H5	0.2848	-1.0190	0.0039
	C4-H6	0.2775	-0.9624	0.0086
	C4-H7	0.2775	-0.9624	0.0086
Propionaldehyde	Bond	ρ (a. u.)	$\nabla^2\rho$ (a. u.)	ε
	C1-O2	0.4286	-0.0677	0.0794
	C1-H3	0.2824	-1.0180	0.0115
	C1-C4	0.2613	-0.6426	0.0589
	C4-C7	0.2771	-0.9554	0.0148
	C4-H5	0.2771	-0.9554	0.0148
	C4-H6	0.2442	-0.5541	0.0023
	C7-H8	0.2829	-0.9997	0.0066
	C7-H9	0.2821	-0.9930	0.0079
	C7-H10	0.2829	-0.9997	0.0066
Trifluoroacetaldehyde	Bond	ρ (a. u.)	$\nabla^2\rho$ (a. u.)	ε
	C1-O2	0.4404	0.0297	0.1087
	C1-H3	0.2865	-1.0540	0.0135
	C1-C4	0.2631	-0.6866	0.0256

	C4-F5	0.2997	-0.2635	0.1330
	C4-F6	0.2867	-0.2925	0.1424
	C4-F7	0.2867	-0.2925	0.1424
Methyl formate	Bond	ρ (a. u.)	$\nabla^2\rho$ (a. u.)	ε
	C1-O2	0.4394	-0.2176	0.1215
	C1-H3	0.2934	-1.1130	0.0342
	C1-O4	0.3151	-0.5237	0.0132
	O41-C5	0.2440	-0.3384	0.0053
	C5-H6	0.2912	-1.0710	0.0374
	C5-H7	0.2939	-1.0920	0.0412
	C5-H8	0.2912	-1.0710	0.0374
N-Methylformamide	Bond	ρ (a. u.)	$\nabla^2\rho$ (a. u.)	ε
	C1-O2	0.4258	-0.3298	0.0978
	C1-H3	0.2864	-1.0510	0.0246
	C1-N4	0.3277	-0.9862	0.1387
	N4-H5	0.3538	-1.8710	0.0512
	N4-C6	0.2599	-0.6644	0.0458
	C6-H7	0.2876	-1.0400	0.0287
	C6-H8	0.2878	-1.0400	0.0262
	C6-H9	0.2876	-1.0400	0.0287
Acrolein	Bond	ρ (a. u.)	$\nabla^2\rho$ (a. u.)	ε
	C2-H1	0.2822	-1.0180	0.0143
	C2-O3	0.4277	-0.1062	0.0868
	C2-C4	0.2754	-0.7219	0.0793
	C4-C5	0.3548	-1.1230	0.2628
	C4-H6	0.2899	-1.0720	0.0049
	C5-H7	0.2910	-1.0820	0.0037
	C5-H8	0.2883	-1.0580	0.0040
Benzaldehyde	Bond	ρ (a. u.)	$\nabla^2\rho$ (a. u.)	ε
	C1-O2	0.4274	-0.1030	0.0814
	C1-H3	0.2830	-1.0230	0.0136
	C1-C4	0.2722	-0.7017	0.0848
	C4-C5	0.3160	-0.9071	0.1576
	C4-H6	0.2888	-1.0580	0.0030
	C5-C7	0.3164	-0.9131	0.1648
	C7-H8	0.2907	-1.0720	0.0074
	C7-C9	0.3169	-0.9158	0.1666
	C9-H10	0.2910	-1.0750	0.0034
	C9-C11	0.3141	-0.9017	0.1576
	C11-H12	0.2909	-1.0740	0.0066
	C11-C13	0.3193	-0.9283	0.1685
	C13-H14	0.2921	-1.0880	0.0042
	C4-C13	0.3135	-0.8966	0.1490

Table S4. Variation in the bond critical bond derived properties for the formyl group in various dimer geometries.

Formaldehyde	$\rho_{C=O}$ (a. u.)	$\nabla^2\rho_{C=O}$ (a. u.)	$\varepsilon_{C=O}$	ρ_{C-H} (a. u.)	$\nabla^2\rho_{C-H}$ (a. u.)	ε_{C-H}
A	0.4276	-0.0298	0.0781	0.2853	-1.0430	0.0107
	-	-	-	0.2899	-1.0830	0.0158
	0.4276	-0.0298	0.0781	0.2853	-1.0430	0.0107
	-	-	-	0.2899	-1.0830	0.0158
B	0.4274	-0.0649	0.0777	0.2875	-1.0610	0.0080
	-	-	-	0.2875	-1.0610	0.0080
	0.4271	-0.0260	0.0713	0.2866	-1.0550	0.0093
	-	-	-	0.2884	-1.0720	0.0124
Acetaldehyde	$\rho_{C=O}$ (a. u.)	$\nabla^2\rho_{C=O}$ (a. u.)	$\varepsilon_{C=O}$	ρ_{C-H} (a. u.)	$\nabla^2\rho_{C-H}$ (a. u.)	ε_{C-H}
A	0.4240	-0.1018	0.0744	0.2872	-1.0580	0.0129
	0.4240	-0.1018	0.0744	0.2872	-1.0580	0.0129
B	0.4252	-0.1081	0.0738	0.2856	-1.0440	0.0066
	0.4243	-0.0831	0.0665	0.2868	-1.0560	0.0128
C	0.4263	-0.0894	0.0790	0.2830	-1.0230	0.0115
	0.4263	-0.0894	0.0790	0.2830	-1.0230	0.0115
D	0.4260	-0.1003	0.0753	0.2846	-1.0360	0.0065
	0.4253	-0.0936	0.0753	0.2840	-1.0310	0.0100
E	0.4257	-0.0954	0.0760	0.2839	-1.0300	0.0092
	0.4257	-0.0954	0.0760	0.2839	-1.0300	0.0092
F	0.4242	-0.0982	0.0728	0.2873	-1.0590	0.0125
	0.4262	-0.0888	0.0781	0.2833	-1.0250	0.0114
G	0.4256	-0.1013	0.0754	0.2850	-1.0400	0.0087
	0.4256	-0.1013	0.0754	0.2850	-1.0400	0.0087
Trifluoroacetaldehyde	$\rho_{C=O}$ (a. u.)	$\nabla^2\rho_{C=O}$ (a. u.)	$\varepsilon_{C=O}$	ρ_{C-H} (a. u.)	$\nabla^2\rho_{C-H}$ (a. u.)	ε_{C-H}
A	0.4364	0.0184	0.0960	0.2897	-1.0860	0.0163
	0.4364	0.0184	0.0960	0.2897	-1.0860	0.0163
C	0.4370	-0.0085	0.0971	0.2888	-1.0750	0.0109
	0.4356	0.0161	0.0894	0.2882	-1.0760	0.0117
B	0.4371	0.0246	0.0973	0.2885	-1.0740	0.0136
	0.4392	0.0225	0.1071	0.2904	-1.0900	0.0166
Propionaldehyde	$\rho_{C=O}$ (a. u.)	$\nabla^2\rho_{C=O}$ (a. u.)	$\varepsilon_{C=O}$	ρ_{C-H} (a. u.)	$\nabla^2\rho_{C-H}$ (a. u.)	ε_{C-H}
A	0.4233	-0.0924	0.0671	0.2865	-1.0530	0.0116
	0.4233	-0.0924	0.0671	0.2865	-1.0530	0.0116
B	0.4247	-0.0970	0.0666	0.2849	-1.0390	0.0063
	0.4232	-0.0767	0.0582	0.2866	-1.0550	0.0118
C	0.4250	-0.0894	0.0678	0.2831	-1.0240	0.0078
	0.4250	-0.0894	0.0678	0.2831	-1.0240	0.0078
D	0.4252	-0.0893	0.0692	0.2825	-1.0190	0.0090
	0.4252	-0.0893	0.0692	0.2825	-1.0190	0.0090
Methyl formate	$\rho_{C=O}$ (a. u.)	$\nabla^2\rho_{C=O}$ (a. u.)	$\varepsilon_{C=O}$	ρ_{C-H} (a. u.)	$\nabla^2\rho_{C-H}$ (a. u.)	ε_{C-H}
A	0.4341	-0.2435	0.1101	0.2972	-1.1530	0.0351
	0.4341	-0.2435	0.1101	0.2972	-1.1530	0.0351
B	0.4355	-0.2386	0.1158	0.2938	-1.1160	0.0336
	0.4355	-0.2386	0.1158	0.2938	-1.1160	0.0336
C	0.4396	-0.2153	0.1208	0.2954	-1.1330	0.0341
	0.4396	-0.2153	0.1208	0.2954	-1.1330	0.0341
N-Methylformamide	$\rho_{C=O}$ (a. u.)	$\nabla^2\rho_{C=O}$ (a. u.)	$\varepsilon_{C=O}$	ρ_{C-H} (a. u.)	$\nabla^2\rho_{C-H}$ (a. u.)	ε_{C-H}

A	0.4181	-0.3683	0.0842	0.2911	-1.0950	0.0236
	0.4181	-0.3683	0.0842	0.2911	-1.0950	0.0236
B	0.4218	-0.3504	0.0916	0.2865	-1.0520	0.0244
	0.4218	-0.3504	0.0916	0.2865	-1.0520	0.0244
C	0.4219	-0.3518	0.0922	0.2849	-1.0400	0.0260
	0.4178	-0.3751	0.0849	0.2883	-1.0680	0.0237
Acrolein	$\rho_{C=O}$ (a. u.)	$\nabla^2\rho_{C=O}$ (a. u.)	$\varepsilon_{C=O}$	ρ_{C-H} (a. u.)	$\nabla^2\rho_{C-H}$ (a. u.)	ε_{C-H}
A	0.4220	-0.1341	0.0743	0.2861	-1.0520	0.0137
	0.4220	-0.1341	0.0743	0.2861	-1.0520	0.0137
B	0.4234	-0.1261	0.0773	0.2828	-1.0230	0.0135
	0.4234	-0.1261	0.0773	0.2828	-1.0230	0.0135
C	0.4215	-0.1332	0.0710	0.2868	-1.0570	0.0136
	0.4236	-0.1254	0.0773	0.2829	-1.0240	0.0130
D	0.4246	-0.1250	0.0805	0.2848	-1.0380	0.0139
	0.4244	-0.1181	0.0777	0.2829	-1.0250	0.0131
E	0.4255	-0.1199	0.0822	0.2819	-1.0160	0.0140
	0.4250	-0.1154	0.0804	0.2833	-1.0280	0.0135
Benzaldehyde	$\rho_{C=O}$ (a. u.)	$\nabla^2\rho_{C=O}$ (a. u.)	$\varepsilon_{C=O}$	ρ_{C-H} (a. u.)	$\nabla^2\rho_{C-H}$ (a. u.)	ε_{C-H}
A	0.4216	-0.1301	0.0690	0.2874	-1.0610	0.0141
	0.4216	-0.1301	0.0690	0.2874	-1.0610	0.0141
B	0.3806	-0.3604	0.576	0.2538	-0.9402	0.0140
	0.3806	-0.3604	0.576	0.2538	-0.9402	0.0140
C	0.4245	-0.1154	0.0757	0.2860	-1.0480	0.0145
	0.4239	-0.1147	0.0730	0.2842	-1.0340	0.0127

Table S5. Geometrical changes observed for various aldehyde dimers.

Formaldehyde	Mono	ΔA	ΔB
C1-O2	1.1939	0.0036	0.0046
C1-H3	1.1028	0.0003	-0.0022
C1-H4	1.1028	-0.0036	-0.0022
O2-C1-H3	121.7295	-0.4753	0.1482
O2-C1-H4	121.7297	-0.7146	0.1480
H3-C1-H4	116.5408	1.1899	-0.3009
C6-O7	1.1939	0.0036	0.0039
C6-H5	1.1028	-0.0036	-0.0015
C6-H8	1.1028	0.0003	-0.0015
O7-C6-H5	121.7295	-0.4753	-0.6718
O7-C6-H8	121.7297	-0.7146	-0.4277
H5-C6-H8	116.5408	1.1899	1.0995

Acetaldehyde	Mono	ΔA	ΔB	ΔC	ΔD	ΔE	ΔF	ΔG
C1-O2	1.1977	0.0052	0.0042	0.0029	0.0035	0.0035	0.0050	0.0039
C1-H3	1.1070	-0.0028	-0.0029	-0.0001	-0.0017	-0.0011	-0.0027	-0.0022
C1-C4	1.4998	-0.0009	-0.0020	-0.0036	-0.0033	-0.0047	-0.0008	-0.0036
C4-H5	1.0858	0.0001	0.0005	0.0012	0.0004	0.0002	0.0002	0.0008
C4-H6	1.0910	0.0052	0.0033	0.0058	0.0044	0.0047	0.0050	0.0063
C4-H7	1.0910	0.0001	0.0006	0.0006	0.0000	0.0000	0.0002	-0.0005
O2-C1-H3	120.1430	-0.1444	0.0901	-0.5392	0.0225	-0.2823	-0.1017	-0.0995
O2-C1-C4	124.3761	-0.6546	-0.0399	0.3191	0.1219	0.2734	-0.6609	-0.0549
H3-C1-C4	115.4809	0.7989	-0.0631	0.2201	-0.1445	0.0088	0.7626	0.1430
C6-O8	1.1977	0.0052	0.0044	0.0029	0.0037	0.0035	0.0030	0.0039
C8-H10	1.1070	-0.0028	-0.0026	-0.0001	-0.0012	-0.0011	-0.0004	-0.0022
C8-C11	1.4998	-0.0009	-0.0021	-0.0036	-0.0049	-0.0047	-0.0036	-0.0036
C11-H12	1.0858	0.0001	0.0000	0.0012	-0.0001	0.0002	0.0018	0.0008
C11-H13	1.0910	0.0000	0.0000	0.0006	-0.0002	-0.0005	0.0004	0.0011
C11-H14	1.0910	0.0001	-0.0001	0.0006	0.0002	0.0000	0.0007	-0.0005
O8-C6-H10	120.1430	-0.1444	-0.5287	-0.5392	-0.4386	-0.2823	-0.5362	-0.0996
O8-C6-C11	124.3761	-0.6546	-0.5512	0.3193	0.2640	9.6785	0.4207	-0.0548
H10-C6-C11	115.4809	0.7990	1.0798	0.2199	0.1739	18.5737	0.1154	0.1430

Proionaldehyde	Mono	ΔA	ΔB	ΔC	ΔD
C1-O2	1.1983	0.0048	0.0037	0.0033	0.0031
C1-H3	1.1069	-0.0023	-0.0025	-0.0003	0.0004
C1-C4	1.5038	-0.0010	-0.0012	-0.0047	-0.0049
C4-C7	1.5181	0.0000	0.0000	-0.0010	-0.0004
C4-H5	1.0942	-0.0001	-0.0030	-0.0006	-0.0005
C4-H6	1.0942	-0.0001	0.0009	0.0003	0.0010
C7-H8	1.0880	0.0001	0.0011	0.0003	0.0008
C7-H9	1.0876	0.0001	0.0002	0.0000	0.0004
C7-H10	1.0880	0.0001	-0.0002	0.0000	-0.0002
O2-C1-H3	120.2918	-119.0886	0.0409	-0.2595	-0.4375
O2-C1-C4	124.3458	-123.2411	-0.0848	0.3773	0.7882
H3-C1-C4	115.3625	-113.8597	0.0259	-0.1179	-0.3507
C1-C4-C7	113.3450	-111.8270	-0.3285	0.1824	0.7205
C11-O12	1.1983	-0.1042	0.0044	0.0033	0.0031
C11-H13	1.1069	-0.0128	-0.0026	-0.0003	0.0004
C11-C14	1.5038	-0.4157	-0.0022	-0.0047	-0.0049
C14-C17	1.5181	-0.4304	0.0001	-0.0010	-0.0004
C14-H15	1.0942	-0.0061	-0.0002	-0.0006	-0.0005
C14-H16	1.0942	-0.0001	0.0001	0.0003	0.0010
C17-H18	1.0880	0.0001	0.0000	0.0003	-0.0002
C17-H19	1.0876	0.0001	0.0000	0.0000	0.0004
C17-H20	1.0880	0.0001	0.0001	0.0000	0.0008
O12-C11-H13	120.2918	-0.0446	-0.5674	-0.2595	-0.4376
O12-C11-C14	124.3458	-0.6206	-0.5142	0.3774	0.7882
H13-C11-C14	115.3625	0.6652	1.0810	-0.1180	4.4917
C11-C14-C17	113.3450	10.3802	0.3064	0.1825	6.5091

Trifluoroacetaldehyde	Mono	ΔA	ΔB	ΔC
C1-O2	1.1865	0.0031	0.0034	0.0023
C1-H3	1.1021	-0.0025	-0.0022	-0.0015
C1-C4	1.5385	-0.0005	0.0023	-0.0005
C4-F5	1.3157	0.0010	0.0085	0.0003
C4-F6	1.3335	-0.0005	-0.0075	-0.0013
C4-F7	1.3335	-0.0005	0.0007	-0.0011
O2-C1-H3	124.2286	-0.5212	0.2283	-0.2768
O2-C1-C4	122.2134	-0.5481	-1.3394	-0.4167
H3-C1-C4	113.5581	1.0693	1.0586	0.6933
C8-O9	1.1865	0.0031	0.0039	0.0011
C8-H10	1.1021	-0.0025	-0.0003	-0.0037
C8-C11	1.5385	-0.0005	-0.0012	0.0028
C11-F5	1.3157	0.0010	0.0004	0.0000
C11-F6	1.3335	-0.0005	-0.0023	0.0039
C11-F7	1.3335	-0.0005	-0.0012	0.0028

O9-C8-H10	124.2286	-0.5212	-0.6288	0.7936
O9-C8-C11	122.2134	-0.5481	-0.5831	-1.0426
H10-C8-C11	113.5581	1.0693	1.2116	0.2490

Methyl formate	Mono	ΔA	ΔB	ΔC
C1-O2	1.1936	0.0046	0.0034	-0.0003
C1-H3	1.0953	-0.0024	-0.0002	-0.0010
C1-O4	1.3300	-0.0007	-0.0064	0.0055
O4-C5	1.4278	-0.0009	0.0048	0.0008
C5-H6	1.0877	0.0000	-0.0015	-0.0002
C5-H7	1.0838	0.0001	-0.0005	0.0002
C5-H8	1.0877	0.0000	-0.0011	-0.0002
O2-C1-H3	124.8918	-0.5674	-0.4867	0.7261
O2-C1-O4	125.3454	-0.7584	0.2410	-0.5506
H3-C1-O4	109.7628	1.3258	0.2457	-0.1755
C1-O4-C5	115.2065	0.2218	0.2970	-0.0497
C9-O10	1.1936	0.0046	0.0034	-0.0003
C9-H11	1.0953	-0.0024	-0.0002	-0.0010
C9-O12	1.3300	-0.0007	-0.0064	0.0055
O12-C13	1.4278	-0.0009	0.0048	0.0008
C13-H14	1.0877	0.0000	-0.0011	-0.0002
C13-H15	1.0838	0.0001	-0.0005	0.0002
C13-H16	1.0877	0.0000	-0.0015	-0.0002
O10-C9-H11	124.8918	-0.5674	-0.4867	0.7261
O10-C9-O12	125.3454	-0.7584	0.2411	-0.5508
H11-C9-O12	109.7628	1.3258	0.2456	-0.1754
C9-O12-C13	115.2065	0.2218	0.2970	-0.0496

N-Methylformamide	Mono	ΔA	ΔB	ΔC
C1-O2	1.2075	0.0075	0.0038	0.0039
C1-H3	1.1011	-0.0021	-0.0002	0.0015
C1-N4	1.3506	-0.0022	-0.0051	-0.0055
N4-C6	1.4491	-0.0005	0.0033	-0.0020
N4-H5	1.0040	0.0000	0.0003	0.0086
C6-H7	1.0887	0.0001	-0.0025	0.0013
C6-H8	1.0855	0.0001	-0.0002	0.0004
C6-H9	1.0887	0.0001	0.0001	0.0000
O2-C1-H3	122.9409	-0.2505	-0.4460	-0.3506
O2-C1-N4	123.9478	-0.8116	0.3546	0.9027
H3-C1-N4	113.1112	1.0622	0.0912	-0.5529
C1-N4-C6	120.7826	0.2544	0.5310	-0.2022
C10-O11	1.2075	0.0075	0.0038	0.0080
C10-H12	1.1011	-0.0021	-0.0002	-0.0012

C10-N13	1.3506	-0.0022	-0.0050	-0.0091
N13-C15	1.4491	-0.0005	0.0033	0.0019
N13-H14	1.0040	0.0000	0.0003	0.0005
C15-H16	1.0887	0.0001	-0.0025	-0.0009
C15-H17	1.0855	0.0001	-0.0002	-0.0004
C15-H18	1.0887	0.0001	0.0001	0.0001
O11-C10-H12	122.9409	-0.2505	-0.4462	-0.6508
O11-C10-N13	123.9478	-0.8116	0.3551	-0.2230
H12-C10-N13	113.1112	1.0622	0.0909	0.8732
C10-N13-C15	120.7826	0.2544	0.5321	0.3049

Acrolein	Mono	ΔA	ΔB	ΔC	ΔD	ΔE
C1-O2	1.2001	0.0053	0.0038	0.0057	0.0030	0.0021
C1-H3	1.1070	-0.0021	-0.0004	-0.0024	-0.0023	0.0003
C1-C4	1.4758	-0.0016	-0.0034	-0.0021	-0.0020	-0.0037
C4-C6	1.3267	0.0006	0.0010	0.0007	0.0015	0.0005
C4-H5	1.0823	0.0001	0.0021	0.0001	0.0003	-0.0009
C6-H7	1.0805	0.0002	0.0000	0.0003	0.0006	0.0000
C6-H8	1.0837	-0.0001	0.0003	0.0001	0.0003	0.0005
O2-C1-H3	121.1260	-0.0892	-0.5701	-0.1740	0.4125	-0.2958
O2-C1-C4	124.1053	-0.4771	0.2433	-0.4804	0.2643	0.1334
H3-C1-C4	114.7687	0.5663	0.3268	0.6544	-0.6768	0.1624
C1-C4-C6	120.2558	-0.3257	-0.7820	-0.4416	-0.7126	0.4520
C9-O10	1.2001	0.0053	0.0038	0.0036	0.0028	0.0022
C9-H11	1.1070	-0.0021	-0.0004	-0.0006	-0.0002	-0.0010
C9-C12	1.4758	-0.0016	-0.0034	-0.0028	-0.0034	-0.0025
C12-C14	1.3267	0.0006	0.0010	0.0012	0.0003	0.0002
C12-H13	1.0823	0.0001	0.0021	0.0024	-0.0018	0.0003
C14-H15	1.0805	0.0001	0.0000	0.0001	0.0030	0.0000
C14-H15	1.0837	-0.0001	0.0003	0.0003	-0.0016	0.0000
O10-C9-H11	121.1260	-0.0891	-0.5701	-0.5406	-0.1988	-0.2085
O10-C9-C12	124.1053	-0.4772	0.2433	0.3871	-0.0056	0.0220
H11-C9-C12	114.7687	0.5664	0.3268	0.1535	0.2044	0.1865
C9-C12-C14	120.2558	-0.3258	-0.7819	-0.8935	-0.1922	-0.1333

Benzaldehyde	Mono	ΔA	ΔB	ΔC
C1-O1	1.2002	0.0053	-1.2002	0.0026
C1-H3	1.1063	-0.0028	-1.1063	-0.0022
C1-C4	1.4820	-0.0007	-1.4820	0.0007
C4-C13	1.3895	0.0007	-1.3895	0.0012
C13-C11	1.3877	-0.0001	-1.3877	0.0005
C11-C9	1.3874	0.0002	-1.3874	0.0000
C9-C7	1.3923	0.0002	-1.3923	0.0005

C7-C5	1.3833	-0.0003	-1.3833	-0.0002
C5-C4	1.3930	0.0001	-1.3930	0.0002
C13-H14	1.0832	-0.0001	-1.0832	-0.0003
C11-H12	1.0807	0.0000	-1.0807	0.0002
C9-H10	1.0813	0.0001	-1.0813	0.0002
C7-H8	1.0808	0.0001	-1.0808	0.0001
C5-H6	1.0814	0.0001	-1.0814	0.0001
O2-C1-H3	120.8007	-0.2054	-120.8007	0.5306
O2-C1-C4	124.4170	-0.6704	-124.4170	-0.2808
H3-C1-C4	114.7823	0.8756	-114.7823	-0.2498
C1-C4-C13	119.4073	-0.0547	-119.4073	-0.3432
C1-C4-C5	120.3709	0.0565	-120.3709	0.1655
C16-C15	1.2002	0.0053	-1.2002	0.0029
C15-H17	1.1063	-0.0028	-1.1063	-0.0010
C15-C18	1.4820	-0.0007	-1.4820	-0.0033
C19-C18	1.3895	0.0007	-1.3895	0.0008
C21-C19	1.3877	-0.0001	-1.3877	-0.0004
C23-C21	1.3874	0.0002	-1.3874	0.0000
C25-C23	1.3923	0.0002	-1.3923	0.0003
C27-C25	1.3833	-0.0003	-1.3833	-0.0006
C18-C27	1.3930	0.0001	-1.3930	0.0002
C19-H20	1.0832	-0.0001	-1.0832	-0.0002
C21-H22	1.0807	0.0000	-1.0807	-0.0001
C23-H24	1.0813	0.0001	-1.0813	-0.0001
C25-H26	1.0808	0.0001	-1.0808	-0.0001
C27-H28	1.0814	0.0001	-1.0814	-0.0001
O16-C15-H17	120.8007	-0.2054	-120.8007	-0.2268
O16-C15-C18	124.4170	-0.6704	-124.4170	-0.0627
H17-C15-C18	114.7823	0.8756	-114.7823	0.2895
C15-C18-C27	119.4073	-0.0547	-119.4073	-0.0464
C15-C18-C19	120.3709	0.0566	-120.3709	-0.0025

Acetaldehyde and trifluoroacetaldehyde dimers: Structure optimization of various dimer geometries reveals six acetaldehyde dimers found as stable minima on the potential energy surface. As in formaldehyde, major structural changes are seen in the bond lengths and angles of the formyl group. Except in dimer C, the lengthening of the C=O bond and the shortening of the formyl C−H bond remains an important signature for all dimers irrespective of their involvement in direct C−H···O interactions. Analysis of electron density and NBO analysis reveals trends

similar to that observed for formaldehyde. Dimer C is a symmetrical cyclic dimer formed by C−H···O interactions involving sp^3 hydrogen atoms. This arrangement positions the two C=O bond dipoles sufficiently away from each other so as not to interfere with the electronic distribution around each other appreciably. This explains the unperturbed C−H distances and negligible change in ρ values (+0.0002 a. u.) at *bcp* for bonds involving formyl hydrogen atoms. The trifluoroacetaldehyde dimers do not show any distinctive behaviour. Considering the enhanced electropositive character of the formyl hydrogen atoms in Trifluoroacetaldehyde one might have expected a noticeable contribution from the highly activated C−H···O interactions to the overall stability of the trifluoroacetaldehyde dimers. However, trifluoroacetaldehyde dimers do not show an appreciable increase in the interaction energy when compared to the analogous acetaldehyde dimers hints at the minor role played by the C−H···O hydrogen bonds in the overall binding of these dimer complexes.

Propionaldehyde, methyl formate and N-methylformamide dimers: Four stable propionaldehyde dimer geometries were observed as stationary point on optimization. These geometries can be categorized based upon the mutual orientation of the carbonyl groups as, planar antiparallel symmetrical (dimer A), orthogonal antiparallel unsymmetrical (dimer B), stacked antiparallel symmetrical (dimer C) and stacked antiparallel unsymmetrical (dimer D). These dimer arrangements are found to be common among aliphatic aldehydes. Some of them are also seen in the case of unsaturated and substituted formyl derivatives. Among these possible arrangements the orthogonal antiparallel dimer B geometry was found to be the most stable for aliphatic aldehydes (except in the case of trifluoroacetaldehyde) followed by the planar antiparallel symmetrical dimer A.

Similar trends, namely the shortening of formyl C−H bonds, elongation of C=O bond lengths, increase in the C=O bond polarity and decrease in the internal delocalization between oxygen n_O and σ^*_{C-H} orbitals of the formyl group were observed for the propionaldehyde dimers. Analogous planar antiparallel symmetrical dimers of methyl formate and N-methylformamide also show a similar behaviour. The formyl hydrogen atom involved in the C−H···O mediated adduct formation shows enhanced electropositive character in methyl formate and N-methylformamide dimers when compared to propionaldehyde. This result in the relatively high stability observed for these dimers (−4.32 and −5.18 kcal/mol respectively). Moreover, the intervening formyl C−H···O interaction distances were found to be relatively shorter (2.38 and 2.31 Å) in these dimers than in the formaldehyde, acetaldehyde and propionaldehyde dimers (~ 2.41-2.44 Å).

Slight changes in the formyl C−H bond lengths were observed for dimer B of N-methylformamide and methyl formate. These dimers were found to associate with weak C−H···O interactions involving the methyl hydrogen atoms. Large C=O···C=O distances between the two formyl fragments in these dimer arrangement result in poor mutual polarization of the formyl groups. As a result, a negligible change in the donor-acceptor delocalization between the n_O and σ^*_{C-H} orbitals was noted for these dimers. Methyl formate dimer C involves a formyl C−H···O interaction (2.47 Å, 3.37 Å, 139°) between the methoxy O-atom and the formyl H-atoms and was found to be the least stable among all possible dimers. No significant changes in geometry and electronic distribution around the formyl group were observed in this case. On the other hand the N-methylformamide dimer C involves mediation by a stronger N−H···O interaction (1.98 Å, 2.92

Å, 153°) and was found to be most stable among the dimers with a stabilization energy of −6.96 kcal/mol.

Acrolein and benzaldehyde dimers: Unsaturated aldehyde dimers do not show unexpected behaviour. The relatively more electropositive character of the formyl H-atom in benzaldehyde dimer results in a stronger formyl C−H···O interactions with short and more linear geometry (2.4 Å, 3.37 Å, 146º). Other electronic properties follow similar trends as found for aliphatic aldehydes.

Table S4. ESPD and NPA derived atomic charges calculated at the optimized geometries at M062X/6-311++G(3df, 3pd) level for the formaldehyde clusters.

Trimer A	Atom	x	y	z	q_{ESP}	q_{NPA}
	C	0.000000	0.000000	0.000000	0.322801	0.31833
	O	0.000000	0.000000	1.201358	-0.341281	-0.56307
	H	0.946436	0.000000	-0.559261	0.030650	0.12239
	H	-0.946433	0.000000	-0.559263	0.030651	0.12239
	H	-2.161151	0.000000	2.344249	-0.022378	0.12533
	C	-3.105604	-0.000184	1.781571	0.444510	0.31318
	O	-3.114827	-0.000185	0.584392	-0.432820	-0.53215
	H	-4.046320	-0.000316	2.357809	-0.010723	0.09363
	H	2.161186	-0.000144	2.344236	-0.022377	0.12533
	C	3.105629	-0.000087	1.781544	0.444510	0.31318
	O	3.114836	-0.000087	0.584365	-0.432819	-0.53215
	H	4.046353	-0.000063	2.357769	-0.010723	0.09363
Trimer B	Atom	x	y	z	q_{ESP}	q_{NPA}
	C	0.000000	0.000000	0.000000	0.346209	0.34048
	O	0.000000	0.000000	1.202889	-0.449851	-0.60577
	H	0.931575	0.000000	-0.581532	0.044662	0.11210
	H	-0.931587	0.000000	-0.581520	0.044639	0.11210
	H	0.000083	4.094200	0.959007	-0.008611	0.10260
	C	0.000014	3.016636	0.730870	0.476866	0.31349
	O	0.000168	2.624869	-0.400707	-0.449581	-0.52210
	H	-0.000197	2.314012	1.578869	-0.011503	0.12655
	H	0.000156	-4.094199	0.959007	-0.008611	0.10260
	C	0.000056	-3.016636	0.730867	0.476866	0.31349
	O	0.000188	-2.624872	-0.400712	-0.449581	-0.52210
	H	-0.000167	-2.314009	1.578864	-0.011503	0.12655

Trimer C	Atom	x	y	z	q_{ESP}	q_{NPA}
	C	0.000000	0.000000	0.000000	0.414953	0.32479
	O	0.000000	0.000000	1.197863	-0.446428	-0.55406
	H	0.935301	0.000000	-0.580687	0.004229	0.10492
	H	-0.935224	-0.010795	-0.580698	0.004264	0.10493
	H	-0.026190	4.102589	0.937269	-0.001126	0.13126
	C	-0.018391	3.023937	0.721343	0.483117	0.32026
	O	-0.016430	2.625865	-0.412056	-0.434922	-0.54394
	H	-0.012483	2.317204	1.564356	-0.001124	0.13126
	O	-0.042998	5.681655	-0.797705	-0.446367	-0.55406
	C	-0.037177	4.932653	-1.732497	0.414682	0.32479
	H	0.900852	4.582189	-2.189952	0.004382	0.10492
	H	-0.969628	4.565347	-2.188119	0.004339	0.10493
Trimer D	Atom	x	y	z	q_{ESP}	q_{NPA}
	C	0.000000	0.000000	0.000000	0.403420	0.32942
	O	0.000000	0.000000	1.201405	-0.452417	-0.56714
	H	0.936151	0.000000	-0.574755	0.020384	0.11657
	H	-0.937196	0.010384	-0.575683	0.028704	0.12051
	H	-1.451503	-3.827510	0.295386	0.002536	0.11127
	C	-0.810665	-2.933545	0.304690	0.439741	0.33367
	O	-0.332793	-2.494500	-0.701732	-0.436561	-0.54001
	H	-0.620722	-2.464513	1.282706	0.008207	0.10867
	C	-2.525917	-0.448927	1.757822	0.373830	0.32913
	O	-2.855470	-1.107026	0.811137	-0.433817	-0.55821
	H	-2.668266	0.641922	1.784046	0.025690	0.10906
	H	-2.077079	-0.900538	2.655094	0.020284	0.10706
Tetramer A	Atom	x	y	z	q_{ESP}	q_{NPA}
	C	0.000000	0.000000	0.000000	0.360679	0.31718
	O	0.000000	0.000000	1.201081	-0.360601	-0.56009
	H	0.946117	0.000000	-0.559908	0.030039	0.12210
	H	-0.947037	0.000515	-0.558799	-0.007926	0.12088
	H	-2.191659	-0.017155	2.313617	-0.007923	0.12088
	C	-3.138636	-0.002327	1.754912	0.360673	0.31717
	O	-3.138554	0.016158	0.553974	-0.360601	-0.56009
	H	-4.084768	-0.004203	2.314791	0.030039	0.12210
	H	2.148424	0.076782	2.342385	-0.021490	0.12611
	C	3.095998	0.081799	1.785280	0.455472	0.31321
	O	3.112262	0.074602	0.588043	-0.442519	-0.53298
	H	4.033582	0.093509	2.366601	-0.013654	0.09358
	H	-5.286384	0.125864	-0.585833	-0.021487	0.12611
	C	-6.233914	0.129081	-0.028638	0.455459	0.31321
	O	-6.250265	0.103606	1.168349	-0.442507	-0.53298
	H	-7.171373	0.156410	-0.609635	-0.013652	0.09358
Tetramer B	Atom	x	y	z	q_{ESP}	q_{NPA}
	C	0.000000	0.000000	0.000000	0.308448	0.33973

	O	0.000000	0.000000	1.202375	-0.434333	-0.60192
	H	0.932284	0.000000	-0.581158	0.047843	0.11138
	H	-0.932286	0.002224	-0.581152	0.047833	0.11137
	H	0.005505	4.104270	1.019605	-0.002395	0.12910
	C	0.003960	3.030501	0.778688	0.488125	0.31864
	O	0.003474	2.658387	-0.363271	-0.437328	-0.54079
	H	0.002891	2.304746	1.605057	-0.008779	0.13153
	H	-0.004818	-4.091599	0.941776	-0.013999	0.10362
	C	-0.003581	-3.012738	0.720360	0.484406	0.31429
	O	-0.003007	-2.613511	-0.408650	-0.444122	-0.52295
	H	-0.002890	-2.316189	1.573516	-0.010282	0.12651
	H	0.940731	4.625180	-2.091898	0.003597	0.10511
	C	0.006375	4.979566	-1.630149	0.418645	0.32531
	O	0.007376	5.717763	-0.686606	-0.451254	-0.55603
	H	-0.928940	4.627501	-2.091732	0.003595	0.10511
Tetramer C	Atom	x	y	z	q_{ESP}	q_{NPA}
	C	0.000000	0.000000	0.000000	0.436131	0.33100
	C	0.000000	0.000000	3.052063	0.436131	0.33100
	H	1.089420	0.000000	-0.134186	0.012384	0.11751
	H	-0.517418	-0.965545	-0.101868	0.013289	0.12228
	H	-0.504684	0.871854	2.609864	0.013289	0.12228
	H	0.009952	-0.069514	4.147467	0.012384	0.11751
	H	-3.234242	0.878007	-0.328336	0.012384	0.11751
	C	-3.010233	0.165157	0.475720	0.436131	0.33100
	H	-2.930131	0.569360	1.495808	0.013289	0.12228
	C	-2.311199	-1.935754	2.576343	0.436131	0.33100
	H	-1.369199	-2.246265	2.100322	0.013289	0.12228
	H	-3.186562	-2.579089	2.419182	0.012384	0.11751
	O	-2.370345	-0.949994	3.261682	-0.461804	-0.57078
	O	-2.885784	-1.010292	0.257219	-0.461804	-0.57078
	O	0.541014	-0.824564	2.364817	-0.461804	-0.57078
	O	-0.606317	1.014253	0.220408	-0.461804	-0.57078
Octamer A	Atom	x	y	z	q_{ESP}	q_{NPA}
	C	0.000000	0.000000	0.000000	0.511856	0.33599
	H	0.000000	0.000000	1.201985	-0.491256	-0.57176
	C	2.503881	0.000000	1.724900	0.421249	0.33866
	H	2.982592	-0.076758	0.623973	-0.482433	-0.58589
	H	-0.014286	2.567679	-0.494692	-0.482542	-0.58592
	C	0.111892	3.024494	0.610973	0.421371	0.33868
	C	3.006245	2.433532	-0.107860	0.511839	0.33600
	H	2.651694	2.969912	0.907700	-0.491276	-0.57175
	H	3.129632	-0.896161	-2.314188	0.510442	0.33598
	H	3.586373	-0.980078	-3.422845	-0.490964	-0.57176
	H	0.567657	-1.011501	-2.824378	-0.482264	-0.58595
	H	0.562626	-0.987241	-4.027079	0.420776	0.33868

O	0.669102	1.524657	-4.495559	-0.490882	-0.57175
O	0.770448	1.977316	-3.386677	0.510254	0.33598
O	3.370319	2.035157	-3.112569	-0.482787	-0.58595
O	3.728611	1.477644	-4.116513	0.422942	0.33868
H	-0.929147	-0.012273	-0.584220	-0.005501	0.12320
C	0.938212	-0.016513	-0.574736	0.000411	0.11739
H	-0.375325	-0.948197	-4.595604	0.025012	0.11796
O	1.497742	-1.032576	-4.603678	0.020835	0.12444
H	2.274497	-0.897165	2.313962	0.024885	0.11797
C	2.303407	0.973812	2.194472	0.020612	0.12444
H	0.220243	4.104070	0.776134	0.024848	0.11796
O	0.094535	2.379585	1.501352	0.020609	0.12443
H	0.778300	1.327125	-2.498972	0.001599	0.11748
C	2.905454	0.079453	-1.857311	0.001338	0.11745
H	2.282984	2.124772	-0.877530	0.000457	0.11740
O	4.064779	2.250129	-0.332928	-0.005510	0.12320
H	2.939522	-1.780372	-1.692229	-0.005110	0.12316
C	4.787311	1.255933	-4.302287	0.024286	0.11797
H	3.011167	1.193699	-4.899848	0.020014	0.12446
O	0.831738	3.057195	-3.199877	-0.005113	0.12316