Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for

The Effect of Hydrogen Bonding on the Planarity of Amides

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Table S1: Performance of different basis sets at B3LYP with BSSE correction for urea dimer

Basis Set	Dimer Energy (Hartree)		Interaction Energy (kJ mol^{-1} per molecule)	
	Uncorrected	BSSE Corrected	Uncorrected	BSSE Corrected
6-31G	-450.408562	-450.403936	-26.1	-21.3
6-31+G(d,p)	-450.594440	-450.593690	-18.3	-18.2
6-31++G(d,p)	-450.594577	-450.593819	-17.8	-17.9
6-31G(2d,2p)	-450.573602	-450.568000	-22.7	-16.4
6-31+G(2d,2p)	-450.611634	-450.611145	-17.2	-17.4
6-31++G(2d,2p)	-450.611852	-450.611367	-17.2	-17.4
6-311G	-450.540353	-450.536954	-24.7	-21.4
6-311+G	-450.558106	-450.557099	-21.9	-21.7
6-311++G	-450.558423	-450.557384	-21.9	-21.7
6-311G(d)	-450.664763	-450.661407	-21.3	-17.9
6-311G(d,p)	-450.688896	-450.685549	-21.1	-17.7
6-311+G(d,p)	-450.710002	-450.709602	-17.8	-18.2
6-311++G(d,p)	-450.710138	-450.709713	-17.8	-18.1
6-311G(2d,2p)	-450.702004	-450.698346	-20.4	-16.5
6-311G+(2d,2p)	-450.722322	-450.721906	-16.8	-17.1
6-311G++(2d,2p)	-450.722396	-450.721983	-16.9	-17.1
6-311G(2df,2pd)	-450.718128	-450.714631	-20.3	-16.7
6-311+G(2df,2pd)	-450.737766	-450.737311	-17.0	-17.2
6-311G++(2df,2pd)	-450.737870	-450.737417	-17.0	-17.2

Figure S1: Two views of the “free” optimised structures of urea dimer.

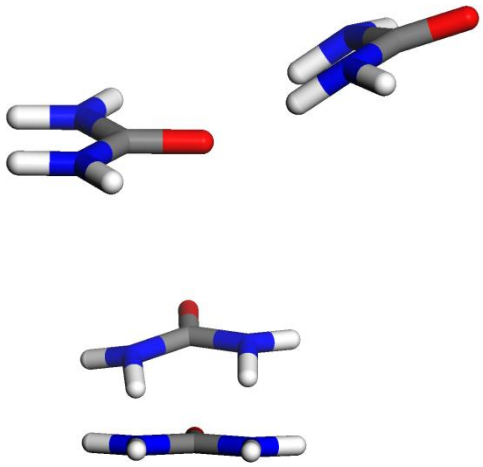

Table S2: Comparison of ab initio and DFT Optimisations for Formamide...HF, all with aug-cc-pVTZ basis set

	r(C–O)	r(C–N)	$OCNH_{syn}$	$OCNH_{anti}$
B3LYP	1.202	1.389	19.72	156.99
CAM-B3LYP	1.197	1.384	19.55	156.80
PW91	1.210	1.395	20.07	156.99
LC-PW91	1.189	1.372	18.90	157.02
ωB97X	1.199	1.386	19.71	156.50
DF-MP2	1.210	1.390	20.67	155.58

Table S3 B3LYP energy data, for comparison against LMP2

	E_{int}	E_{def}	E_{bind}
Formamide...HF	-5.37	+1.21	-4.16

Table S4: Optimized cartesian coordinates for all species

Formamide

O	1.196022	0.228083	0.000000
C	0.000358	0.418780	0.000000
H	-0.441561	1.430275	0.000000
N	-0.941217	-0.558326	0.000000
H	-0.654759	-1.523324	0.000000
H	-1.920620	-0.337925	0.000000

Formamide...HF

O	1.156725	0.190215	0.037075
C	-0.026821	0.396997	0.066532
H	-0.464462	1.408013	0.095786
N	-0.987263	-0.604366	0.133302
H	-0.661418	-1.518816	-0.154482
H	-1.910176	-0.364658	-0.200892
H	-1.361731	-0.987719	1.917527
F	-1.550922	-1.181362	2.819197

Formamide...(HF)2

O	1.227776	0.126369	0.024849
C	0.044499	0.392841	0.051049
H	-0.330410	1.424342	0.085768
N	-0.939087	-0.559581	0.095662
H	-0.659325	-1.495589	-0.168719
H	-1.866561	-0.283353	-0.191576
H	-1.354748	-0.973467	1.943975
F	-1.555342	-1.173165	2.835937
H	2.235067	1.468696	-0.028420
F	2.651533	2.317476	-0.081809

Formamide...NCH syn 0

O	1.189214	0.282220	0.000000
C	-0.009719	0.466781	0.000000
H	-0.448244	1.481399	0.000000
N	-0.952304	-0.504623	0.000000
H	-0.676969	-1.478085	0.000000
H	-1.927373	-0.266908	0.000000
N	-0.048814	-3.587232	0.000000
C	0.273071	-4.685499	0.000000
H	0.572994	-5.708613	0.000000

Formamide...NCH syn 15

O	1.197333	0.243323	0.026021
C	-0.002361	0.417682	-0.009444
H	-0.448566	1.428337	-0.043933
N	-0.936514	-0.562998	-0.039579
H	-0.656659	-1.525948	0.094578
H	-1.911578	-0.329172	0.012635
N	-0.094370	-3.579510	0.704021
C	0.205058	-4.652043	0.968418
H	0.483998	-5.651166	1.214717

Formamide...NCH syn 30

O	1.196054	0.261919	0.027359
C	-0.004135	0.425707	-0.022654
H	-0.457990	1.431734	-0.081456
N	-0.929716	-0.565671	-0.062780
H	-0.648859	-1.508753	0.171179
H	-1.902876	-0.331780	0.027197
N	-0.295512	-3.401295	1.370672
C	-0.071478	-4.403091	1.877083
H	0.137204	-5.336204	2.348768

Formamide...NCH anti 180

O	1.252533	0.230246	0.000000
C	0.051166	0.407397	0.000000
H	-0.395943	1.416736	0.000000
N	-0.883944	-0.569062	0.000000
H	-0.585161	-1.530128	0.000000
H	-1.868762	-0.353022	0.000000
N	-4.003170	0.222175	0.000000
C	-5.112524	0.503604	0.000000
H	-6.146256	0.765818	0.000000

Formamide...NCH anti 165

O	1.200961	0.224488	-0.017389
C	0.001648	0.413231	-0.011849
H	-0.435453	1.426645	0.012874
N	-0.943576	-0.554612	-0.044462
H	-0.648186	-1.516402	-0.006326
H	-1.916985	-0.334818	0.101050
N	-3.994164	0.176958	0.704704
C	-5.076698	0.436567	0.970543
H	-6.085384	0.678475	1.218287

Formamide...NCH anti 150

O	1.205182	0.209970	-0.039465
C	0.008721	0.412365	-0.028291
H	-0.416430	1.430542	0.007197
N	-0.948797	-0.546396	-0.071426
H	-0.652186	-1.507022	-0.003865
H	-1.898975	-0.326772	0.186032
N	-3.808546	-0.017589	1.371284
C	-4.816872	0.168842	1.879976
H	-5.756285	0.342530	2.353927

Formamide...(NCH)2 0/180

O	1.238302	0.278715	0.000000
C	0.034299	0.450946	0.000000
H	-0.409518	1.463262	0.000000
N	-0.902325	-0.520386	0.000000
H	-0.615350	-1.489392	0.000000
H	-1.882681	-0.289158	0.000000
N	0.026663	-3.653557	0.000000
C	0.352059	-4.751043	0.000000
H	0.655111	-5.773029	0.000000
N	-4.068402	0.294324	0.000000
C	-5.176974	0.579659	0.000000
H	-6.209612	0.845302	0.000000

Formamide...(NCH)2 30/150

O	-1.436595	2.523421	-0.346802
C	-0.333125	2.119540	-0.038222
H	0.577289	2.722268	-0.209801
N	-0.065573	0.939458	0.570796
H	-0.801820	0.246827	0.599277
H	0.881208	0.592158	0.566195
N	-2.034361	-1.669030	0.060047
C	-2.715806	-2.571930	-0.116761
H	-3.350264	-3.412529	-0.281343
N	2.810190	-0.596822	0.009943
C	3.805391	-1.128498	-0.184172
H	4.732186	-1.623610	-0.364921

Formamide...(NCH)2 -30/150

O	1.243053	0.287804	-0.007804
C	0.039551	0.460513	-0.009224
H	-0.404559	1.471985	0.022812
N	-0.896547	-0.511829	-0.006498
H	-0.617511	-1.474995	-0.119616
H	-1.868285	-0.292947	0.135947
N	-0.230199	-3.421307	-1.435738
C	0.000353	-4.427955	-1.930297
H	0.214997	-5.365095	-2.390625
N	-3.823077	0.047330	1.428280
C	-4.836326	0.240925	1.925097
H	-5.779878	0.421213	2.387666

Urea

O	0.000000	0.000000	0.035329
C	0.000000	0.000000	1.251358
N	1.161515	0.020066	2.000658
N	-1.161515	-0.020066	2.000658
H	1.987009	0.232838	1.466225
H	1.136119	0.414533	2.925984
H	-1.987009	-0.232838	1.466225
H	-1.136119	-0.414533	2.925984

Urea...HF

O	-0.007693	-0.022562	1.352717
C	0.008062	0.005783	0.143854
N	0.025731	1.154609	-0.601626
N	0.030871	-1.179535	-0.630569
H	0.194010	1.998064	-0.079439
H	0.386421	1.136843	-1.540604
H	-0.259272	-1.968832	-0.068506
H	-0.482247	-1.135856	-1.501318
H	1.706230	-1.576964	-1.053644
F	2.603625	-1.789825	-1.280249

Urea...NCH syn 0

O	-0.100731	-0.050321	0.078195
C	-0.097382	-0.010876	1.295298
N	1.048825	0.031874	2.049734
N	-1.271894	0.015230	2.037518
H	1.913186	0.129689	1.537841
H	1.021038	0.408599	2.980298
H	-2.089057	-0.209089	1.494672
H	-1.259250	-0.383337	2.961836
N	3.862011	0.025085	0.449738
C	4.856984	0.022697	-0.116129
H	5.783660	0.020449	-0.643087

Urea...NCH syn 30

O	-0.098423	-0.052483	0.072316
C	-0.096818	-0.045407	1.289373
N	1.055881	-0.049015	2.045763
N	-1.270479	-0.045544	2.030048
H	1.885009	0.229787	1.540056
H	1.003112	0.313298	2.983458
H	-2.086500	-0.273677	1.487114
H	-1.253717	-0.443200	2.954586
N	3.685446	1.378693	0.745117
C	4.608053	1.879642	0.288770
H	5.467280	2.346133	-0.136222

Urea...NCH anti 180

O	-0.050776	0.037428	-0.107728
C	-0.022688	0.027610	1.111773
N	1.137815	0.078056	1.835007
N	-1.175106	-0.023920	1.877064
H	1.976847	0.261955	1.316851
H	1.145037	0.205788	2.833034
H	-1.995577	-0.301662	1.366865
H	-1.117514	-0.344242	2.829066
N	0.860527	0.034596	5.084386
C	0.763256	0.019262	6.224825
H	0.672529	0.005130	7.287419

Urea...NCH anti 150

O	-2.630698	-0.332517	-0.399571
C	-1.519426	-0.036529	0.004252
N	-0.579225	-0.969008	0.384272
N	-1.096720	1.275713	0.112453
H	-0.819760	-1.910480	0.124319
H	0.400022	-0.734903	0.310876
H	-1.836449	1.953876	0.050569
H	-0.350930	1.495794	0.750356
N	2.558669	-0.163353	-0.027506
C	3.658567	0.119011	-0.171853
H	4.683239	0.382136	-0.306311

Urea...(NCH)2 0/180

O	-1.016960	2.313668	-0.007158
C	-0.025212	1.601098	-0.006397
N	-0.069860	0.239185	-0.002034
N	1.257562	2.136377	-0.044035
H	-0.977653	-0.194952	-0.039657
H	0.756623	-0.326060	-0.088932
H	1.293613	3.112740	0.193449
H	2.023638	1.578512	0.294847
N	-3.033424	-1.150462	0.006782
C	-4.069940	-1.636453	0.009921
H	-5.034971	-2.088949	0.012726
N	2.820471	-1.354915	-0.001354
C	3.822957	-1.907754	-0.001051
H	4.756683	-2.422803	-0.000906

Urea...(NCH)2 30/150

O	-0.811881	2.441890	-0.252275
C	0.127317	1.726489	0.053588
N	-0.011072	0.507238	0.674236
N	1.440710	2.094971	-0.201116
H	-0.944087	0.125591	0.618450
H	0.722846	-0.174142	0.548034
H	1.554263	3.070537	-0.417472
H	2.171222	1.687798	0.358273
N	-2.790140	-1.207409	0.033417
C	-3.746243	-1.797501	-0.187199
H	-4.636447	-2.346573	-0.392325
N	2.309901	-1.784022	0.033812
C	3.109303	-2.573303	-0.186968
H	3.853886	-3.308289	-0.392232

Urea...(NCH)2 -30/150

O	-0.829658	2.228463	-0.556920
C	0.028754	1.515782	-0.061701
N	-0.036777	0.151189	-0.030763
N	1.196298	2.042914	0.476982
H	-0.872707	-0.269932	-0.398342
H	0.795295	-0.409368	0.046773
H	1.158986	3.037882	0.618559
H	1.666125	1.522297	1.198433
N	-3.106351	-1.229910	0.093299
C	-4.150098	-1.699509	0.135516
H	-5.121380	-2.136512	0.174792
N	2.819159	-1.483406	-0.084338
C	3.812621	-2.052008	-0.102999
H	4.737889	-2.581516	-0.120352

Urea dimer

Urea trimer 1

C	0.000000	2.782500	1.527000
O	0.000000	2.782500	2.788400
N	0.811900	3.594400	0.827200
H	1.522484	4.069099	1.355266
H	1.011679	3.420176	-0.142276
N	-0.811900	1.970600	0.827200
H	-1.522482	1.495899	1.355265
H	-1.011676	2.144821	-0.142277
C	0.000000	2.782500	6.211000
O	0.000000	2.782500	7.472400
N	0.811900	3.594400	5.511200
H	1.283769	4.313731	6.025464
H	0.736320	3.653203	4.506870
N	-0.811900	1.970600	5.511200
H	-1.283773	1.251272	6.025463
H	-0.736326	1.911803	4.506869
C	0.000000	2.782500	10.895000
O	0.000000	2.782500	12.156400
N	0.811900	3.594400	10.195200
H	1.532361	4.052580	10.719747
H	0.886307	3.506075	9.192174
N	-0.811900	1.970600	10.195200
H	-1.532361	1.512419	10.719745
H	-0.886299	2.058918	9.192173

Urea trimer 2

C	0.000000	2.782500	6.211000
O	0.000000	2.782500	7.472400
N	0.811900	3.594400	5.511200
H	1.464493	4.203301	5.987225
H	0.867550	3.552674	4.510307
N	-0.811900	1.970600	5.511200
H	-1.455672	1.352640	5.987482
H	-0.859307	2.003089	4.509599
C	-2.782500	0.000000	7.841000
O	-2.782500	0.000000	6.579600
N	-3.594400	0.811900	8.540800
H	-4.046041	1.529890	8.002524
H	-3.407300	1.026604	9.504374
N	-1.970600	-0.811900	8.540800
H	-1.251186	-1.261472	8.002580
H	-1.757393	-0.625785	9.504883
C	2.782500	5.565000	7.841000
O	2.782500	5.565000	6.579600
N	1.970600	6.376900	8.540800
H	1.264467	6.815921	8.011910
H	1.756401	6.191046	9.505831
N	3.594400	4.753100	8.540800
H	4.046925	4.035921	8.002539
H	3.407297	4.538027	9.504254

Urea pentamer

C	5.312881	-0.009837	-0.006027
O	4.051486	-0.007291	-0.003412
N	6.010358	-1.159445	-0.009019
H	5.473464	-1.994446	0.147939
H	6.971510	-1.181171	0.284222
N	6.014998	1.136948	-0.005937
H	5.481014	1.974451	-0.159313
H	6.975469	1.155050	-0.301541
C	0.628901	-0.000383	0.003684
O	-0.632494	0.002162	0.006300
N	1.326377	-1.149993	0.000692
H	0.850889	-2.040134	0.003926
H	2.333212	-1.124875	0.002031
N	1.331018	1.146401	0.003775
H	0.858992	2.038425	0.012320
H	2.337723	1.117219	0.008650
C	-4.055109	0.002008	0.006315
O	-5.316532	-0.002508	0.001850
N	-3.357603	-1.140540	0.010404
H	-3.886000	-1.937624	-0.291117
H	-2.357966	-1.112044	-0.164496
N	-3.352962	1.155854	0.013486
H	-3.879051	1.940711	-0.323794
H	-2.356544	1.118787	-0.177854
C	-0.993140	3.937944	0.012345
O	0.268255	3.935398	0.009730
N	-1.690560	3.937810	1.161993
H	-1.121918	3.763746	1.974098
H	-2.593680	3.489648	1.187647
N	-1.695315	3.940902	-1.134400
H	-1.149562	4.075787	-1.967611
H	-2.633925	4.301819	-1.153027
C	-1.009045	-3.932132	0.001783
O	0.252350	-3.934677	-0.000833
N	-1.706465	-3.932265	1.151430
H	-1.138894	-3.761832	1.964945
H	-2.612181	-3.490428	1.179172
N	-1.711220	-3.929174	-1.144963
H	-1.165860	-4.062727	-1.978668
H	-2.651484	-4.285590	-1.165605

Glycyl glycine

C	-0.042911	0.588086	0.157995
N	-1.110149	-0.374994	0.378960
C	1.211750	-0.135711	-0.314699
O	1.157621	-1.169236	-0.963201
N	2.387165	0.466342	-0.008904
C	3.648211	-0.070704	-0.453540
C	4.775178	0.794513	0.051262
O	4.640563	1.780617	0.730652
O	5.971189	0.327589	-0.352101
H	-1.022738	-1.123958	-0.299202
H	-2.020765	0.049584	0.272918
H	-0.268280	1.335602	-0.617106
H	0.167488	1.139033	1.078145
H	2.421810	1.292091	0.567530
H	3.799017	-1.092535	-0.095935
H	3.702566	-0.123834	-1.543848
H	6.652328	0.917965	0.003015

Glycyl glycine...HF

C	-0.030233	0.585527	0.119714
C	1.222403	-0.111688	-0.380644
N	2.353257	0.700868	-0.456208
C	3.644478	0.076978	-0.722414
C	4.704243	0.716795	0.142179
O	5.923666	0.227482	-0.131759
N	-0.986184	-0.392921	0.607491
O	1.230527	-1.260310	-0.762854
O	4.489477	1.561223	0.974787
H	-0.934137	-1.232191	0.042126
H	-1.930781	-0.036730	0.569876
H	-0.389778	1.191517	-0.725075
H	0.233112	1.288262	0.915190
H	2.415720	1.428360	0.248744
H	3.596468	-0.992839	-0.512363
H	3.934258	0.178170	-1.769535
H	6.560679	0.669414	0.449685
H	2.055352	1.777318	-1.882584
F	1.959675	2.338622	-2.637725

Glycyl glycine...H2O

C	-0.132992	0.504907	0.167787
N	-1.097845	-0.490173	0.605945
C	1.133426	-0.186825	-0.319247
O	1.115318	-1.297656	-0.816224
N	2.280519	0.553273	-0.225639
C	3.562048	-0.033540	-0.563207
C	4.666227	0.813432	0.016991
O	4.496571	1.788989	0.705698
O	5.877792	0.342432	-0.320754
H	-1.019145	-1.311196	0.016240
H	-2.043937	-0.140856	0.545460
H	-0.477931	1.124938	-0.673145
H	0.105038	1.188605	0.986955
H	2.321639	1.319602	0.431165
H	3.646819	-1.051246	-0.174426
H	3.701316	-0.100023	-1.643354
H	6.543064	0.922044	0.079354
O	2.783200	2.371468	-2.792115
H	2.355825	2.025677	-1.998810
H	2.897050	3.312607	-2.630970