Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Data

Computational Insights into the Photocyclization of Diclofenac in Solution: Effects of Halogen and Hydrogen Bondings

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Table S1. Calculated geometrical properties of **DCF** obtained at the TD-DFT/B3LYP/6-31G+(d) theoretical level.

medium	C2-C3							C13-H16							N10-H11						
	B.L. (Å)	Charges						B.L. (Å)	Charges						B.L. (Å)	Charges					
		C2			C3				C13			H16				N10			H11		
		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO
vacuum	1.416	-0.363	0.040	0.133	0.692	0.010	-0.087	1.087	-0.477	-0.050	-0.233	0.191	0.043	0.248	1.012	-0.640	-0.098	-0.646	0.430	0.108	0.440
water	1.416	-0.411	0.037	0.129	0.699	0.008	-0.090	1.087	-0.397	-0.054	-0.246	0.208	0.048	0.256	1.012	-0.538	-0.097	-0.646	0.454	0.117	0.450
Ethanol	1.416	-0.453	0.038	0.130	0.717	0.008	-0.091	1.087	-0.393	-0.054	-0.244	0.207	0.048	0.255	1.013	-0.535	-0.097	-0.646	0.453	0.116	0.450
Isoprop.	1.416	-0.469	0.038	0.131	0.727	0.008	-0.091	1.087	-0.389	-0.053	-0.243	0.207	0.048	0.255	1.013	-0.534	-0.097	-0.647	0.453	0.115	0.450
DCM	1.416	-0.533	0.038	0.132	0.765	0.008	-0.091	1.087	-0.372	-0.052	-0.240	0.205	0.047	0.254	1.013	-0.530	-0.098	-0.647	0.452	0.114	0.449
Ethyl. Ac.	1.416	-0.578	0.038	0.132	0.797	0.007	-0.092	1.087	-0.354	-0.051	-0.238	0.203	0.046	0.254	1.013	-0.529	-0.098	-0.648	0.451	0.113	0.448
1,4-Dioxane	1.416	-0.265	0.040	0.132	0.647	0.010	-0.087	1.087	-0.471	-0.051	-0.236	0.198	0.045	0.251	1.012	-0.650	-0.097	-0.645	0.439	0.112	0.444
n-Hexane	1.416	-0.284	0.040	0.132	0.656	0.010	-0.087	1.087	-0.471	-0.051	-0.236	0.197	0.044	0.251	1.012	-0.648	-0.097	-0.646	0.437	0.111	0.444

N10-C12							C12-C13						
B.L. (Å)	Charges						B.L. (Å)	Charges					
	N10			C12				C12			C13		
	M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO
1.427	-0.640	-0.098	-0.646	-0.642	0.037	0.145	1.402	-0.642	0.037	0.145	-0.477	-0.050	-0.233
1.423	-0.538	-0.097	-0.646	-0.747	0.034	0.154	1.403	-0.747	0.034	0.154	-0.397	-0.054	-0.246
1.424	-0.535	-0.097	-0.646	-0.750	0.034	0.154	1.403	-0.750	0.034	0.154	-0.393	-0.054	-0.244
1.425	-0.534	-0.097	-0.647	-0.757	0.035	0.154	1.403	-0.757	0.035	0.154	-0.389	-0.053	-0.243
1.427	-0.530	-0.098	-0.647	-0.770	0.035	0.153	1.402	-0.770	0.035	0.153	-0.372	-0.052	-0.240
1.428	-0.529	-0.098	-0.648	-0.779	0.036	0.152	1.402	-0.779	0.036	0.152	-0.354	-0.051	-0.238
1.425	-0.650	-0.097	-0.645	-0.634	0.036	0.147	1.403	-0.634	0.036	0.147	-0.471	-0.051	-0.236
1.426	-0.648	-0.097	-0.646	-0.638	0.037	0.146	1.403	-0.638	0.037	0.146	-0.471	-0.051	-0.236

Table S2. Calculated geometrical properties of **DCF•** obtained at the TD-DFT/B3LYP/6-31G+(d) theoretical level.

medium	C2-C3						C13-H16							N10-H11					
	B.L. (Å)	Charges						B.L. (Å)	Charges						B.L. (Å)	Charges				
		C2			C3				C13			H16				N10			H11		
		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO
vacuum	1.392	-0.802	0.036	0.062	1.042	-0.028	0.122	1.087	-0.287	-0.044	-0.230	0.191	0.045	0.248	1.013	-0.489	-0.098	-0.653	0.434	0.112	0.442
water	1.391	-0.817	0.033	0.058	1.196	-0.030	-0.330	1.087	-0.350	-0.049	-0.243	0.211	0.052	0.257	1.014	-0.441	-0.101	-0.651	0.461	0.117	0.446
Ethanol	1.391	-0.814	0.034	0.058	1.185	-0.030	0.115	1.087	-0.348	-0.049	-0.242	0.210	0.051	0.257	1.014	-0.465	-0.100	-0.651	0.441	0.117	0.445
Isoprop.	1.391	-0.813	0.034	0.059	1.180	-0.030	0.116	1.087	-0.347	-0.049	-0.242	0.209	0.051	-0.237	1.014	-0.466	-0.100	-0.651	0.440	0.117	0.445
DCM	1.391	-0.810	0.044	0.059	1.160	-0.029	0.116	1.087	-0.341	-0.052	-0.241	0.207	0.057	0.255	1.014	-0.466	-0.129	-0.651	0.439	0.130	0.445
Ethyl. Ac.	1.391	-0.809	0.045	0.060	1.145	-0.028	0.117	1.087	-0.337	-0.052	-0.239	0.205	0.056	0.254	1.014	-0.471	-0.129	-0.651	0.438	0.129	0.444
1,4-Dioxane	1.391	-0.813	0.045	0.061	1.098	-0.027	0.120	1.087	-0.318	-0.051	-0.235	0.198	0.054	0.251	1.014	-0.480	-0.128	-0.651	0.435	0.127	0.443
n-Hexane	1.391	-0.813	0.035	0.061	1.089	-0.028	0.120	1.087	-0.314	-0.046	-0.234	0.197	0.047	0.250	1.014	-0.481	-0.098	-0.652	0.435	0.114	0.442

N10-C12						C12-C13						
B.L. (Å)	Charges					B.L. (Å)	Charges					
	N10			C12			C12			C13		
	M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO
1.432	-0.489	-0.098	-0.653	-0.228	0.040	0.147	1.398	-0.228	0.040	0.147	-0.287	-0.044	-0.230
1.432	-0.441	-0.101	-0.651	-0.401	0.034	0.143	1.400	-0.401	0.034	0.143	-0.350	-0.049	-0.243
1.432	-0.465	-0.100	-0.651	-0.396	0.034	0.143	1.400	-0.396	0.034	0.143	-0.348	-0.049	-0.242
1.432	-0.394	-0.100	-0.651	-0.394	0.034	0.144	1.400	-0.394	0.034	0.144	-0.347	-0.049	-0.242
1.432	-0.466	-0.129	-0.651	-0.385	0.042	0.144	1.400	-0.385	0.042	0.144	-0.341	-0.052	-0.241
1.432	-0.471	-0.129	-0.651	-0.378	0.043	0.144	1.400	-0.378	0.043	0.144	-0.337	-0.052	-0.239
1.432	-0.480	-0.128	-0.651	-0.348	0.045	0.146	1.399	-0.348	0.045	0.146	-0.318	-0.051	-0.235
1.432	-0.481	-0.098	-0.652	-0.343	0.038	0.146	1.400	-0.343	0.038	0.146	-0.314	-0.046	-0.234

Table S3. Calculated geometrical properties of **CCA** obtained at the TD-DFT/B3LYP/6-31G+(d) theoretical level.

medium	C2-C3						C13-H16							N10-H11						
	B.L. (Å)	Charges						B.L. (Å)	Charges						B.L. (Å)	Charges					
		C2			C3				C13			H16				N10			H11		
		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO
vacuum	1.421	-0.684	0.032	0.137	1.052	-0.022	-0.060	---	1.168	-0.024	-0.094	---	---	---	1.015	-0.454	-0.072	-0.563	0.457	0.111	0.467
water	1.423	-0.612	0.028	0.133	1.002	-0.027	-0.064	---	1.122	-0.030	-0.102	---	---	---	1.015	-0.458	-0.073	-0.563	0.458	0.112	0.468
Ethanol	1.423	-0.616	0.028	0.133	1.005	-0.027	-0.064	---	1.125	-0.030	-0.101	---	---	---	1.015	-0.458	-0.073	-0.563	0.458	0.112	0.468
Isoprop.	1.423	-0.618	0.028	0.133	1.007	-0.026	-0.064	---	1.126	-0.030	-0.101	---	---	---	1.015	-0.458	-0.073	-0.563	0.458	0.112	0.468
DCM	1.423	-0.625	0.029	0.133	1.013	-0.026	-0.063	---	1.131	-0.029	-0.100	---	---	---	1.015	-0.457	-0.073	-0.563	0.458	0.112	0.468
Ethyl. Ac.	1.422	-0.631	0.029	0.134	1.017	-0.025	-0.063	---	1.135	-0.029	-0.100	---	---	---	1.015	-0.457	-0.073	-0.563	0.458	0.112	0.468
1,4-Dioxane	1.422	-0.656	0.031	0.135	1.035	-0.024	-0.062	---	1.152	-0.026	-0.097	---	---	---	1.015	-0.455	-0.073	-0.563	0.457	0.111	0.467
n-Hexane	1.422	-0.661	0.031	0.136	1.038	-0.024	-0.061	---	1.155	-0.026	-0.096	---	---	---	1.015	-0.455	-0.072	-0.563	0.457	0.111	0.467

N10-C12							C12-C13						
B.L. (Å)	Charges						B.L. (Å)	Charges					
	N10			C12				C12			C13		
	M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO
1.388	-0.454	-0.072	-0.563	-0.309	0.037	0.189	1.421	-0.309	0.037	0.189	1.168	-0.024	-0.094
1.389	-0.458	-0.073	-0.563	-0.263	0.034	0.185	1.421	-0.263	0.034	0.185	1.122	-0.030	-0.102
1.389	-0.458	-0.073	-0.563	-0.266	0.034	0.186	1.421	-0.266	0.034	0.186	1.125	-0.030	-0.101
1.388	-0.458	-0.073	-0.563	-0.267	0.034	0.186	1.421	-0.267	0.034	0.186	1.126	-0.030	-0.101
1.389	-0.457	-0.073	-0.563	-0.272	0.034	0.186	1.421	-0.272	0.034	0.186	1.131	-0.029	-0.100
1.389	-0.457	-0.073	-0.563	-0.275	0.035	0.187	1.421	-0.275	0.035	0.187	1.135	-0.029	-0.100
1.389	-0.455	-0.073	-0.563	-0.292	0.036	0.188	1.421	-0.292	0.036	0.188	1.152	-0.026	-0.097
1.389	-0.455	-0.072	-0.563	-0.295	0.036	0.188	1.421	-0.295	0.036	0.188	1.155	-0.026	-0.096

Table S4. Calculated geometrical properties of **CCA •** obtained at the TD-DFT/B3LYP/6-31G+(d) theoretical level.

medium	C2-C3						C13-H16							N10-H11						
	B.L. (Å)	Charges						B.L. (Å)	Charges						B.L. (Å)	Charges					
		C2			C3				C13			H16				N10			H11		
		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO
vacuum	1.409	-0.890	0.045	0.144	0.745	-0.012	-0.035	---	-0.198	-0.016	-0.330	---	---	---	1.019	-0.440	0.117	-0.586	0.460	0.117	0.466
water	1.410	-0.798	0.041	0.141	0.721	-0.013	-0.036	---	-0.137	-0.016	-0.333	---	---	---	1.018	-0.445	-0.109	-0.590	0.459	0.116	0.464
Ethanol	1.410	-0.805	0.041	0.142	0.723	-0.013	-0.036	---	-0.141	-0.016	-0.333	---	---	---	1.018	-0.445	-0.108	-0.590	0.459	0.116	0.464
Isoprop.	1.410	-0.807	0.042	0.142	0.724	-0.013	-0.036	---	-0.142	-0.016	-0.333	---	---	---	1.018	-0.445	-0.108	-0.589	0.459	0.116	0.464
DCM	1.410	-0.819	0.030	0.142	0.726	-0.013	-0.036	---	-0.149	-0.015	-0.333	---	---	---	1.018	-0.444	-0.080	-0.589	0.459	0.106	0.465
Ethyl. Ac.	1.410	-0.828	0.042	0.142	0.730	-0.013	-0.035	---	-0.156	-0.016	-0.333	---	---	---	1.018	-0.444	-0.108	-0.589	0.459	0.116	0.465
1,4-Dioxane	1.410	-0.860	0.032	0.144	0.738	-0.013	-0.035	---	-0.178	-0.015	-0.333	---	---	---	1.019	-0.442	-0.078	-0.587	0.460	0.107	0.465
n-Hexane	1.410	-0.866	0.044	0.144	0.740	-0.012	-0.035	---	-0.182	-0.016	0.331	---	---	---	1.019	-0.442	-0.106	-0.587	0.460	0.117	0.465

N10-C12							C12-C13						
B.L. (Å)	Charges						B.L. (Å)	Charges					
	N10			C12				C12			C13		
	M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO		M.Q.	H.Q.	NBO	M.Q.	H.Q.	NBO
1.386	-0.440	0.117	-0.586	0.790	0.057	0.234	1.516	0.790	0.057	0.234	-0.198	-0.016	-0.330
1.388	-0.445	-0.109	-0.590	0.766	0.055	0.233	1.515	0.766	0.055	0.233	-0.137	-0.016	-0.333
1.388	-0.445	-0.108	-0.590	0.768	0.055	0.234	1.515	0.768	0.055	0.234	-0.141	-0.016	-0.333
1.388	-0.445	-0.108	-0.589	0.769	0.055	0.234	1.515	0.769	0.055	0.234	-0.142	-0.016	-0.333
1.388	-0.444	-0.080	-0.589	0.772	0.047	0.234	1.515	0.772	0.047	0.234	-0.149	-0.015	-0.333
1.387	-0.444	-0.108	-0.589	0.774	0.055	0.234	1.515	0.774	0.055	0.234	-0.156	-0.016	-0.333
1.387	-0.442	-0.078	-0.587	0.783	0.048	0.234	1.515	0.783	0.048	0.234	-0.178	-0.015	-0.333
1.386	-0.442	-0.106	-0.587	0.785	0.056	0.234	1.515	0.785	0.056	0.234	-0.182	-0.016	0.331

Table S5. Calculated charges of **DCF** • as complexed with water molecule(s) obtained at the TD-DFT/B3LYP/6-31G+(d) theoretical level.

	A				B				AB			
	ESM		ESM + IEFPCM		ESM		ESM + IEFPCM		ESM		ESM + IEFPCM	
Atom	M.Q.	H.Q.	M.Q.	H.Q.	M.Q.	H.Q.	M.Q.	H.Q.	M.Q.	H.Q.	M.Q.	H.Q.
C2	-0.0910	0.0388	-0.1300	0.0385	-1.7380	0.0512	-1.5720	0.0479	-0.6890	0.0429	-0.8680	0.0415
C3	0.1010	-0.0257	0.2330	-0.0217	0.8420	-0.0308	0.8550	-0.0399	0.9530	-0.0288	0.8410	-0.0277
C12	-0.5680	0.0447	-0.2980	0.0410	-0.2590	0.0564	-0.2290	0.0473	-0.7710	0.0471	-0.7620	0.0409
C13	0.5690	-0.0532	0.5360	-0.0574	0.5980	-0.0505	0.4190	-0.0545	0.7730	-0.0468	0.6240	-0.0477
N10	-0.4320	-0.0872	-0.4340	-0.0871	-0.4670	-0.1310	-0.5150	-0.1352	-0.4100	-0.0988	-0.4630	-0.1011
H11	0.4700	0.0912	0.4680	0.0883	0.5450	0.0947	0.5340	0.0906	0.5530	0.0854	0.5410	0.0813
H16	0.2030	0.0401	0.2130	0.0406	0.1910	0.0505	0.2040	0.0539	0.1930	0.0453	0.2100	0.0488
O26	-0.4320	-0.2617	-0.4790	-0.2874	-0.4740	-0.2552	-0.5040	-0.2694	-0.4720	-0.2462	-0.5000	-0.2594