Electronic Supplementary Material for PCCP

Photophysics of xanthine:

Computational study of the radiationless decay mechanisms

Electronic Supplementary Information

Shohei Yamazaki,[*,a] Andrzej L. Sobolewski[b] and Wolfgang Domcke[a]

[a] *Department of Chemistry, Technical University of Munich, D-85747 Garching, Germany*

[b] *Institute of Physics, Polish Academy of Sciences, PL-02668 Warsaw, Poland*

E-mail: shohei.yamazaki@ch.tum.de

Table S1: Cartesian coordinates of ground-state minimum geometries of the 7H-diketo tautomer of xanthine, optimized with the CC2 method (in au)

Atom	x	y	z	Atom	x	y	z
		cc-pVDZ				aug-cc-pVDZ	
N	-1.506943383	0.000000000	-2.852316841	N	-1.513220604	0.000000000	-2.862416966
C	1.088264632	0.000000000	-3.463624361	C	1.083464207	0.000000000	-3.462050347
N	2.673501237	0.000000000	-1.360325282	N	2.676885464	0.000000000	-1.365923256
C	1.725666868	0.000000000	1.068307761	C	1.726465103	0.000000000	1.065048610
C	-0.870230881	0.000000000	1.504918812	C	-0.871847658	0.000000000	1.509381756
C	-2.746799325	0.000000000	-0.480357808	C	-2.735074277	0.000000000	-0.478721059
N	-1.094382500	0.000000000	4.108991415	N	-1.094770763	0.000000000	4.117625954
C	1.310740691	0.000000000	5.063729805	C	1.314057901	0.000000000	5.078724698
N	3.100228854	0.000000000	3.260901496	N	3.100512450	0.000000000	3.263861532
O	1.859727326	0.000000000	-5.652896046	O	1.859310428	0.000000000	-5.667397332
O	-5.070761794	0.000000000	-0.266856376	O	-5.075033607	0.000000000	-0.263761090
H	1.684289206	0.000000000	7.089028967	H	1.690914484	0.000000000	7.099285236
H	-2.664488456	0.000000000	-4.395852653	H	-2.673403528	0.000000000	-4.402129387
H	4.566435511	0.000000000	-1.691848048	H	4.568272406	0.000000000	-1.703573287
H	-2.750549869	0.000000000	5.083133709	H	-2.746307818	0.000000000	5.097661530
		cc-pVTZ				aug-cc-pVTZ	
N	-1.503159981	0.000000000	-2.836558970	N	-1.504514141	0.000000000	-2.838535510
C	1.074122935	0.000000000	-3.441673424	C	1.073137809	0.000000000	-3.439234055
N	2.655555362	0.000000000	-1.358371789	N	2.657821447	0.000000000	-1.359459637
C	1.712729529	0.000000000	1.055310451	C	1.714452018	0.000000000	1.054724670
C	-0.860477791	0.000000000	1.498212976	C	-0.859788089	0.000000000	1.498010516
C	-2.718827158	0.000000000	-0.470835408	C	-2.714379103	0.000000000	-0.470477926
N	-1.082468750	0.000000000	4.087374279	N	-1.083422496	0.000000000	4.086659139
C	1.308283762	0.000000000	5.034204955	C	1.307254147	0.000000000	5.037891510
N	3.077363001	0.000000000	3.234997758	N	3.075908417	0.000000000	3.236626481
O	1.837594469	0.000000000	-5.624396887	O	1.836249908	0.000000000	-5.627089002
O	-5.032950622	0.000000000	-0.252915628	O	-5.033706640	0.000000000	-0.252452452
H	1.684455710	0.000000000	7.033551857	H	1.681460799	0.000000000	7.039144122
H	-2.656265409	0.000000000	-4.363693365	H	-2.658333215	0.000000000	-4.367880179
H	4.532964131	0.000000000	-1.690237452	H	4.536893558	0.000000000	-1.695091962
H	-2.722922432	0.000000000	5.056995915	H	-2.725392814	0.000000000	5.057847595

Table S2: Cartesian coordinates of ground-state minimum geometries of the 9H-diketo tautomer of xanthine, optimized with the CC2 method (in au)

Atom	x	y	z	Atom	x	y	z
		cc-pVDZ				aug-cc-pVDZ	
N	-1.508176328	0.000000000	-2.838451627	N	-1.509045638	0.000000000	-2.853154200
C	1.045406984	0.000000000	-3.501127654	C	1.050607237	0.000000000	-3.493484921
N	2.673397435	0.000000000	-1.405872332	N	2.678033657	0.000000000	-1.401049746
C	1.696669009	0.000000000	1.003421302	C	1.694615230	0.000000000	1.010422194
C	-0.870654500	0.000000000	1.595774010	C	-0.877265843	0.000000000	1.592561126
C	-2.741279332	0.000000000	-0.426021068	C	-2.734213294	0.000000000	-0.435176215
N	-1.226346802	0.000000000	4.196614810	N	-1.232914117	0.000000000	4.199355680
C	1.092150797	0.000000000	5.136057341	C	1.085117787	0.000000000	5.154571346
N	2.955467623	0.000000000	3.269451375	N	2.952186873	0.000000000	3.282379156
O	1.833762889	0.000000000	-5.684477414	O	1.849764227	0.000000000	-5.690743611
O	-5.057041107	0.000000000	-0.279636096	O	-5.064133824	0.000000000	-0.295242320
H	1.591443968	0.000000000	7.134396030	H	1.572939067	0.000000000	7.151580347
H	-2.704873820	0.000000000	-4.352257425	H	-2.701465874	0.000000000	-4.368251445
H	4.551160309	0.000000000	-1.806301575	H	4.555102521	0.000000000	-1.801891653
H	4.856508835	0.000000000	3.544687719	H	4.851655811	0.000000000	3.558094536
		cc-pVTZ				aug-cc-pVTZ	
N	-1.497435839	0.000000000	-2.828895343	N	-1.496417136	0.000000000	-2.832258985
C	1.042443694	0.000000000	-3.472808916	C	1.044760049	0.000000000	-3.468729895
N	2.655991454	0.000000000	-1.390905432	N	2.658478373	0.000000000	-1.388364877
C	1.678229221	0.000000000	1.001605104	C	1.677751665	0.000000000	1.004028478
C	-0.868749199	0.000000000	1.582372318	C	-0.870789433	0.000000000	1.580911083
C	-2.717782193	0.000000000	-0.429655613	C	-2.715146560	0.000000000	-0.432634751
N	-1.218579632	0.000000000	4.168978849	N	-1.221150141	0.000000000	4.167718282
C	1.079254221	0.000000000	5.110308894	C	1.074984337	0.000000000	5.115240848
N	2.931583028	0.000000000	3.253450639	N	2.928872732	0.000000000	3.257322977
O	1.831307369	0.000000000	-5.646665866	O	1.836149810	0.000000000	-5.646732817
O	-5.023204383	0.000000000	-0.286990671	O	-5.025044318	0.000000000	-0.294265787
H	1.566153136	0.000000000	7.085920535	H	1.559993763	0.000000000	7.092915502
H	-2.683123061	0.000000000	-4.331106705	H	-2.681816238	0.000000000	-4.337472295
H	4.519376140	0.000000000	-1.784535035	H	4.524031510	0.000000000	-1.782436853
H	4.816333615	0.000000000	3.526427013	H	4.815414585	0.000000000	3.532042376

Table S3: Cartesian coordinates of $^1\pi\pi^*$ minimum geometries of the 7H-diketo tautomer of xanthine, optimized with the CC2 and CASSCF methods (in au)

Atom	x	y	z	Atom	x	y	z
		CC2/cc-pVDZ				CC2/aug-cc-pVDZ	
N	-1.479328010	-0.024813427	-2.944066610	N	-1.484308093	0.141071939	-2.963983443
C	1.056132873	0.004248399	-3.468633921	C	1.052056648	-0.002382258	-3.458154007
N	2.654320251	0.051387124	-1.275707230	N	2.663659037	-0.086192603	-1.282924828
C	1.766577397	0.039907141	1.125149111	C	1.772069814	0.131475560	1.120564442
C	-0.951674692	0.056890272	1.493442781	C	-0.941289370	0.048609924	1.486263503
C	-2.760831101	0.014340016	-0.500984996	C	-2.752124609	-0.095354814	-0.513395886
N	-1.232883481	0.165755201	4.106795845	N	-1.185642464	0.055593426	4.066539959
C	1.319403166	-0.160333375	5.129897305	C	1.313297058	-0.095970859	5.132072852
N	3.137112102	-0.045094537	3.266771689	N	3.103889760	0.028427796	3.314383511
O	2.045941512	-0.023404339	-5.573544585	O	2.060783984	-0.040386781	-5.578733136
O	-5.119061353	-0.039257225	-0.396481633	O	-5.150572073	-0.050363130	-0.369697470
H	1.699493901	0.277805894	7.112676011	H	1.641015265	-0.024582580	7.158723891
H	-2.638487715	-0.070307208	-4.485672856	H	-2.634201789	0.137334030	-4.511071887
H	4.557761428	0.009563592	-1.625323141	H	4.555129517	-0.227645555	-1.655670228
H	-2.747353308	-0.732822256	4.905997437	H	-2.852944743	-0.212481639	4.985019071
		CASSCF/cc-pVDZ				CASSCF/aug-cc-pVDZ[a]	
N	-1.480555544	0.118385908	-2.917547117	N	-1.450076050	0.000000000	-2.938404108
C	1.053192568	0.006227787	-3.402347845	C	1.095858171	0.000000000	-3.389526015
N	2.614936279	-0.057458071	-1.261534754	N	2.641010543	0.000000000	-1.248524122
C	1.746363526	0.079955987	1.096924866	C	1.709185479	0.000000000	1.102848810
C	-0.947333516	0.274948613	1.508729749	C	-0.968965265	0.000000000	1.481083403
C	-2.676184828	0.035145492	-0.541360277	C	-2.686858570	0.000000000	-0.579817354
N	-1.280348934	-0.288474742	4.121545491	N	-1.262418292	0.000000000	4.057790153
C	1.248239044	0.214426413	5.029987835	C	1.215619573	0.000000000	5.131219742
N	3.133930665	-0.137898477	3.179019674	N	3.096090895	0.000000000	3.258505819
O	1.957683133	-0.046862081	-5.470930810	O	2.014848812	0.000000000	-5.463905046
O	-4.953732103	-0.125927922	-0.407706128	O	-4.976480659	0.000000000	-0.471073130
H	1.669980676	-0.136429391	6.996828392	H	1.565611277	0.000000000	7.120306306
H	-2.604503883	0.098055333	-4.438434482	H	-2.548792857	0.000000000	-4.470683786
H	4.472777020	-0.253663602	-1.580893323	H	4.505881455	0.000000000	-1.550555037
H	-2.558529382	0.835771390	4.964480643	H	-2.890239129	0.000000000	4.985687313

[a] Optimized with C_s symmetry constraint.

Table S4: Cartesian coordinates of $^1\pi\pi^*$ minimum geometries of the 9H-diketo tautomer of xanthine, optimized with the CC2 and CASSCF methods (in au)

Atom	x	y	z	Atom	x	y	z
		CC2/cc-pVDZ				CC2/aug-cc-pVDZ	
N	-1.210072172	0.794028478	-2.954753890	N	-1.298752768	0.661431356	-2.953613137
C	1.229668752	-0.052489372	-3.330262328	C	1.169607389	-0.051070882	-3.368157980
N	2.625207807	-0.164709260	-1.030960545	N	2.624225114	-0.188024712	-1.102645601
C	1.672382355	0.897035144	1.172901814	C	1.707617017	0.806010151	1.131484073
C	-1.099732536	0.244230407	1.495785476	C	-1.058091809	0.213704743	1.514458574
C	-2.693413830	0.155974625	-0.672140320	C	-2.700783543	0.098832703	-0.617419351
N	-1.471857365	-0.509626226	3.936696566	N	-1.421681128	-0.406542376	3.995448724
C	0.741337486	-0.376434938	5.113410305	C	0.825781068	-0.302021017	5.133695367
N	2.784393055	0.175062309	3.519401264	N	2.837689595	0.124109251	3.471227310
O	2.253284626	-0.634381619	-5.342380116	O	2.205021769	-0.498906685	-5.426328700
O	-4.993845857	-0.273134989	-0.889898442	O	-5.042888978	-0.237426275	-0.747521012
H	1.020591150	-0.774782130	7.118883965	H	1.129624053	-0.628016983	7.144079702
H	-2.283913496	0.721262725	-4.560883493	H	-2.404204416	0.630280260	-4.536045399
H	4.323775840	-1.101122646	-1.108579545	H	4.388146399	-0.972338504	-1.280670298
H	4.321337149	1.116773026	4.211811316	H	4.502092065	0.882856134	4.068528902
		CASSCF/cc-pVDZ				CASSCF/aug-cc-pVDZ	
N	-1.417183108	0.236327747	-2.936382792	N	-1.415732350	0.215874740	-2.945290161
C	1.142534617	-0.070744553	-3.371577417	C	1.147086315	-0.069147530	-3.366615928
N	2.650594894	-0.156068111	-1.241118087	N	2.656980299	-0.153333266	-1.236762756
C	1.753759665	0.676160222	1.087004073	C	1.750390183	0.664617476	1.091585346
C	-0.964917495	0.244796114	1.508722809	C	-0.970828039	0.239372221	1.507390967
C	-2.677470324	0.099813330	-0.618307914	C	-2.678458664	0.096621092	-0.626318793
N	-1.492787325	-0.264148425	4.017131932	N	-1.497931732	-0.262182010	4.019406299
C	0.962846300	-0.358433362	5.175047525	C	0.956855129	-0.350053775	5.187001029
N	2.893310343	-0.014871368	3.378781947	N	2.890826488	-0.015756457	3.387677459
O	1.993231713	-0.259464373	-5.458114171	O	2.007007166	-0.247246975	-5.457674619
O	-4.942107478	-0.091657219	-0.506802473	O	-4.947529657	-0.081594206	-0.522433425
H	1.174803433	0.390084186	7.063836771	H	1.164833233	0.409226328	7.067234606
H	-2.498468013	0.135939707	-4.484693818	H	-2.487855467	0.126700614	-4.494094532
H	4.504739928	-0.159598117	-1.605187253	H	4.506452971	-0.155487296	-1.598665384
H	4.442484439	0.919464442	3.930585534	H	4.444160525	0.904312774	3.934414952

Table S5: Cartesian coordinates of $^1n\pi^*$ minimum geometries of the 7H-diketo tautomer of xanthine, optimized with the CC2 and CASSCF methods (in au)

Atom	x	y	z	Atom	x	y	z
		CC2/cc-pVDZ				CC2/aug-cc-pVDZ	
N	-1.410081543	-0.208399151	-2.944426469	N	-1.436414803	-0.151716543	-2.952573611
C	1.218112376	-0.005637828	-3.413214064	C	1.191868028	-0.006811721	-3.426847596
N	2.706647323	-0.110564800	-1.260597974	N	2.699641363	-0.054833316	-1.281358219
C	1.711814013	-0.047939396	1.177397734	C	1.719389623	-0.041327478	1.162931397
C	-0.966603138	0.012397649	1.519816748	C	-0.955422304	0.048072747	1.528874682
C	-2.526068615	0.040810282	-0.542592463	C	-2.509999404	0.141729655	-0.536463642
N	-1.244460017	0.089153355	4.135690959	N	-1.222849239	0.054637042	4.146874633
C	1.184199100	0.038065617	5.167663337	C	1.214725211	0.015697129	5.176370372
N	2.996745030	-0.031815919	3.394789368	N	3.013618147	-0.047162374	3.379330335
O	2.053904028	0.173267487	-5.574864469	O	2.032416510	0.096769062	-5.608687097
O	-5.235346673	0.004595965	-0.666390439	O	-5.249653745	-0.062810203	-0.598587890
H	1.500473890	0.071693922	7.200808298	H	1.543809510	0.002493890	7.203649682
H	-2.477578173	0.249586736	-4.482695299	H	-2.510685480	0.268770106	-4.495282749
H	4.603918602	0.026764571	-1.542382835	H	4.597783885	-0.002319830	-1.581493097
H	-2.900030749	0.015116288	5.100254065	H	-2.873455016	0.083269418	5.120975414
		CASSCF/cc-pVDZ				CASSCF/aug-cc-pVDZ	
N	-1.464429632	0.095466229	-2.923323749	N	-1.467892750	0.101317198	-2.927804584
C	1.115165827	-0.001116560	-3.399408883	C	1.112704486	0.001763763	-3.397313442
N	2.647111516	-0.163335493	-1.313690055	N	2.648341317	-0.167247987	-1.316854932
C	1.655406558	-0.070871188	1.101713578	C	1.652340805	-0.076811036	1.099391702
C	-0.894799462	0.166861747	1.506480110	C	-0.892869138	0.169339182	1.506827835
C	-2.606023231	0.535919154	-0.550782330	C	-2.606278882	0.548044916	-0.553193823
N	-1.140246444	0.219901854	4.095192299	N	-1.139611704	0.226785680	4.098205114
C	1.232181734	-0.013115194	5.058409949	C	1.232707741	-0.010472620	5.063518579
N	2.969840858	-0.175704942	3.295169368	N	2.968552843	-0.182686155	3.298823591
O	1.922328836	0.039998367	-5.515176463	O	1.920877502	0.041022172	-5.520676679
O	-4.993111901	-0.516376707	-0.418337746	O	-4.987042083	-0.531804340	-0.413869354
H	1.590904433	-0.068815723	7.059008386	H	1.591412155	-0.064937915	7.059888620
H	-2.453810225	0.583637839	-4.457979468	H	-2.452256638	0.584009286	-4.460970087
H	4.506365546	-0.255184261	-1.607148972	H	4.502766358	-0.259179858	-1.614099798
H	-2.740689960	0.270561552	5.084696276	H	-2.732710994	0.304311941	5.090150544

Table S6: Cartesian coordinates of $^1n\pi^*$ minimum geometries of the 9H-diketo tautomer of xanthine, optimized with the CC2 and CASSCF methods (in au)

Atom	x	y	z	Atom	x	y	z
		CC2/cc-pVDZ				CC2/aug-cc-pVDZ	
N	-1.450275584	0.247144580	-2.870396800	N	-1.466798881	0.188444503	-2.886744635
C	1.144266935	-0.060960767	-3.436314819	C	1.129654038	-0.063025578	-3.441834693
N	2.685961518	-0.130776060	-1.316173155	N	2.687126518	-0.113246832	-1.324414603
C	1.801316036	0.623728492	1.089033637	C	1.805375307	0.611715862	1.086219069
C	-0.911975169	0.357017435	1.570687597	C	-0.907136277	0.360725743	1.572367299
C	-2.466767488	0.133138504	-0.450801973	C	-2.451250591	0.117846587	-0.452762471
N	-1.387297020	-0.053547523	4.169696285	N	-1.374159353	-0.030613895	4.176338235
C	0.889624262	-0.274518316	5.132762037	C	0.908381488	-0.274539589	5.147025640
N	2.890099886	-0.187035635	3.399601765	N	2.894037370	-0.190554078	3.397300187
O	1.901548628	-0.228490858	-5.629551628	O	1.906384985	-0.203813976	-5.646830664
O	-5.135586043	-0.251893702	-0.575731361	O	-5.166399835	-0.233816574	-0.541478710
H	1.276683804	-0.544659358	7.144308988	H	1.295552326	-0.538925693	7.154343482
H	-2.619964265	0.182705635	-4.398758197	H	-2.637256807	0.232606650	-4.413912047
H	4.553800046	0.021884423	-1.764647562	H	4.551849030	0.028495976	-1.780918291
H	4.630097042	0.415743742	3.972358139	H	4.678638732	0.283212491	3.938397971
		CASSCF/cc-pVDZ				CASSCF/aug-cc-pVDZ	
N	-1.435555490	0.375001055	-2.903237911	N	-1.430848539	0.387281135	-2.910800099
C	1.093277927	0.036411469	-3.406354312	C	1.098545483	0.039126565	-3.399684937
N	2.681590282	-0.034252108	-1.323363616	N	2.687659093	-0.032669881	-1.317218433
C	1.617517094	-0.077773998	1.062750674	C	1.613095204	-0.097725531	1.068134967
C	-0.891137467	0.195784102	1.556907447	C	-0.895419891	0.173456910	1.553453007
C	-2.627807527	0.592551539	-0.519036881	C	-2.623328276	0.593572054	-0.525835587
N	-1.300560651	0.221366754	4.134923008	N	-1.308316253	0.221507099	4.136218019
C	0.927981707	-0.023507915	5.128949407	C	0.919273516	-0.010731881	5.137924744
N	2.811127811	-0.189992788	3.343942316	N	2.806127707	-0.183165191	3.354777263
O	1.897138708	-0.148456470	-5.514635858	O	1.908697996	-0.147869398	-5.513153949
O	-4.898636575	-0.686258758	-0.497640799	O	-4.901007848	-0.685808642	-0.517939872
H	1.334471480	-0.113712569	7.120145355	H	1.318879353	-0.090364291	7.126575416
H	-2.474229044	0.679281228	-4.450970533	H	-2.462391297	0.687495708	-4.457508071
H	4.391684729	-0.755054147	-1.661201193	H	4.379293601	-0.785544117	-1.656550575
H	4.657243488	-0.353018702	3.673539568	H	4.646405673	-0.352969444	3.690407801

Table S7: Cartesian coordinates of $^1\pi\sigma^*$ minimum geometries of the 7H- and 9H-diketo tautomers of xanthine, optimized with the CC2 and CASSCF methods (in au)

Atom	x	y	z	Atom	x	y	z
	7H-diketo, CC2/aug-cc-pVDZ				7H-diketo, CASSCF/aug-cc-pVDZ		
N	-1.502951093	0.000000000	-2.909563195	N	-1.471202791	0.000000000	-2.901112055
C	1.077256721	0.000000000	-3.445120100	C	1.098261883	0.000000000	-3.376528129
N	2.684984459	0.000000000	-1.267033000	N	2.676543426	0.000000000	-1.255165851
C	1.769188100	0.000000000	1.093424161	C	1.761410621	0.000000000	1.095586664
C	-0.923543880	0.000000000	1.514876256	C	-0.922302701	0.000000000	1.523476300
C	-2.770774380	0.000000000	-0.549984774	C	-2.727230342	0.000000000	-0.591825482
N	-1.167453332	0.000000000	4.044110079	N	-1.175262725	0.000000000	4.012313348
C	1.275759541	0.000000000	5.056533019	C	1.201952458	0.000000000	5.013129400
N	3.099852668	0.000000000	3.305580009	N	3.014999558	0.000000000	3.266772463
O	1.993313561	0.000000000	-5.572341610	O	1.958735729	0.000000000	-5.458447148
O	-5.083673270	0.000000000	-0.343847439	O	-4.975561454	0.000000000	-0.407966011
H	1.572949760	0.000000000	7.090907425	H	1.491235693	0.000000000	7.020757708
H	-2.637468775	0.000000000	-4.474185536	H	-2.558481709	0.000000000	-4.446768017
H	4.592409906	0.000000000	-1.606722824	H	4.538918871	0.000000000	-1.579816187
H	-2.851623832	0.000000000	5.075473374	H	-2.810642545	0.000000000	5.070165591
	9H-diketo, CC2/aug-cc-pVDZ				9H-diketo, CASSCF/aug-cc-pVDZ		
N	-1.512333691	0.000000000	-2.881972545	N	-1.476205406	0.000000000	-2.891129628
C	1.067519102	0.000000000	-3.460352232	C	1.090236169	0.000000000	-3.380979105
N	2.711408387	0.000000000	-1.298189034	N	2.692412986	0.000000000	-1.254545495
C	1.760885642	0.000000000	1.031332124	C	1.751055967	0.000000000	1.049853657
C	-0.926870026	0.000000000	1.579062507	C	-0.934597913	0.000000000	1.558683296
C	-2.763893374	0.000000000	-0.510047008	C	-2.721662633	0.000000000	-0.573280008
N	-1.317865652	0.000000000	4.097617089	N	-1.333071974	0.000000000	4.033777467
C	1.056006294	0.000000000	5.095858431	C	0.961742520	0.000000000	5.065069781
N	2.944982197	0.000000000	3.316318610	N	2.864105321	0.000000000	3.286133846
O	1.931385084	0.000000000	-5.604488903	O	1.945977303	0.000000000	-5.459450865
O	-5.079786512	0.000000000	-0.322933766	O	-4.974008889	0.000000000	-0.404849655
H	1.471471620	0.000000000	7.111929166	H	1.356755534	0.000000000	7.053660503
H	-2.665714990	0.000000000	-4.433928136	H	-2.566366178	0.000000000	-4.434595020
H	4.659219867	0.000000000	-1.577353152	H	4.575582071	0.000000000	-1.552107879
H	4.929391387	0.000000000	3.531931487	H	4.773407131	0.000000000	3.587715715

Table S8: Cartesian coordinates of $^1\pi\pi^*$–S_0 conical intersection geometries of the 7H- and 9H-diketo tautomers of xanthine, optimized with the CASSCF/cc-pVDZ method (in au)

Atom	x	y	z	Atom	x	y	z
		$CI_{7H}(1)$				$CI_{7H}(2)$	
N	-1.707346489	-0.192428251	-2.637756242	N	-1.604728222	-0.157418956	-2.734379216
C	0.763289389	0.037630611	-3.454060258	C	0.901684622	0.024394282	-3.415225556
N	2.588959709	0.332015555	-1.574598678	N	2.622970553	0.278366906	-1.431443672
C	1.943833396	0.218617071	0.903527068	C	1.864172911	0.218765548	1.000183109
C	-0.673939829	0.513833937	1.592263470	C	-0.795937697	0.303389370	1.604968337
C	-2.655978919	-0.046218185	-0.161409105	C	-2.697817458	-0.056833160	-0.307180800
N	-0.672642874	0.962467515	4.324903248	N	-0.992116790	0.678564817	4.294990625
C	1.216420974	-0.893923111	4.428954847	C	1.178766798	-0.837038987	4.545952670
N	3.320275523	-0.355376690	2.868551526	N	3.251586970	-0.173409833	3.032199087
O	1.333013416	-0.061143670	-5.633207684	O	1.601842607	-0.059858377	-5.556723413
O	-4.874059808	-0.289868243	0.271103455	O	-4.944373346	-0.202970107	-0.051592466
H	0.995158397	-2.733997480	5.295063837	H	1.126164672	-2.622316660	5.540366431
H	-2.980496458	-0.424902126	-4.016035559	H	-2.806727600	-0.347301327	-4.181591520
H	4.377797147	0.044449592	-2.113453733	H	4.449266902	0.083141455	-1.878330557
H	-2.301680323	0.336576555	5.088016713	H	-0.632504590	2.496729114	4.753223907
		$CI_{9H}(1)$				$CI_{9H}(2)$	
N	-1.448742856	-0.067043666	-2.798014575	N	-1.517939219	-0.006803575	-2.764174370
C	1.135898821	-0.157880095	-3.236585040	C	1.054021242	-0.124003910	-3.306175061
N	2.682899030	0.038541648	-1.128443951	N	2.644226109	0.019080974	-1.256990363
C	1.651483386	1.054302476	1.114093109	C	1.739023997	0.920549845	1.067658868
C	-0.972288637	0.376398157	1.654835602	C	-0.887125290	0.413232686	1.683964545
C	-2.732258321	0.175701865	-0.517178717	C	-2.710130454	0.150437597	-0.432907062
N	-1.416137539	-0.281880835	4.034777349	N	-1.334695422	-0.115830280	4.125829435
C	1.077409229	-1.191550358	4.166591096	C	1.085370611	-1.163327502	4.203832064
N	2.923769065	0.584575834	3.581809519	N	3.120886065	0.341721607	3.377295921
O	1.965176963	-0.384217682	-5.323709770	O	1.789651014	-0.351572738	-5.429690102
O	-4.985654656	0.143233004	-0.394274694	O	-4.956437272	0.067090016	-0.213511312
H	1.417366787	-3.217176560	4.199699047	H	1.325038584	-3.190505577	4.401876400
H	-2.515281573	-0.269459231	-4.347972715	H	-2.644656068	-0.210287558	-4.270496852
H	4.403783194	0.656822002	-1.621788623	H	4.452246491	0.343339521	-1.699073467
H	4.628866384	-0.217411031	3.339330374	H	3.311670213	1.917271266	4.430164403

Table S9: Cartesian coordinates of $^1n\pi^*$–S_0 conical intersection geometries of the 7H-diketo tautomer of xanthine, optimized with the CASSCF/cc-pVDZ method (in au)

Atom	x	y	z	Atom	x	y	z
		$CI_{7H}(3)$				$CI_{7H}(4)$	
N	-1.397393443	0.360095662	-2.911895999	N	-1.432339093	-0.202982686	-2.863416195
C	1.224440300	-0.033283039	-3.303492603	C	1.185240658	-0.008189663	-3.316288269
N	2.607494885	-0.561912176	-1.165288679	N	2.699188992	0.139596414	-1.212923457
C	1.697126865	-0.128074214	1.239279350	C	1.771382808	0.191796825	1.221988617
C	-1.071083499	0.308764560	1.578277913	C	-1.000874802	0.583170312	1.562502760
C	-2.371619620	0.120973383	-0.495556536	C	-2.347950084	0.006112977	-0.405949065
N	-1.512587496	-0.175345479	4.220894755	N	-1.414324637	0.549565734	4.240458133
C	0.987043040	0.434159730	5.187561166	C	0.940569066	-0.534183451	5.133245961
N	2.908050933	-0.112770293	3.294439772	N	2.931730103	-0.341465041	3.231205737
O	2.122970207	0.180594244	-5.350913744	O	1.974772707	0.052193798	-5.421801697
O	-4.877991897	-0.365036559	-1.154858280	O	-4.915868491	-0.396526447	-1.026694734
H	1.201048713	2.235902044	6.143153124	H	0.837358860	-2.388604883	6.008900825
H	-1.924655614	1.925754348	-3.852200138	H	-2.402352289	0.771414535	-4.179873952
H	4.469444845	-0.759009416	-1.426102936	H	4.549028450	-0.117159382	-1.503797051
H	-1.774174495	-2.038391223	4.504732647	H	-1.524529042	2.344539330	4.856264642
		$CI_{7H}(5)$					
N	-1.179984126	0.861562700	-2.817042590				
C	1.385607855	0.125814372	-3.134589100				
N	2.635618273	-0.299281249	-0.925153085				
C	1.403327518	-0.157818067	1.385282848				
C	-1.117798157	0.300248900	1.545199057				
C	-2.560852673	0.793112067	-0.704598555				
N	-1.621049236	0.386381699	4.098512083				
C	0.615206793	-0.067061900	5.279363485				
N	2.494542449	-0.380493329	3.705079505				
O	2.294203777	-0.008701801	-5.188792804				
O	-4.121205989	-1.298909236	-2.074075683				
H	0.774231812	-0.160014111	7.305192124				
H	-2.024934714	1.355751492	-4.436604458				
H	4.452832506	-0.793857019	-1.028005532				
H	-3.296704096	0.610408155	4.924516860				

Table S10: Cartesian coordinates of $^1n\pi^*$–S_0 conical intersection geometries of the 9H-diketo tautomer of xanthine, optimized with the CASSCF/cc-pVDZ method (in au)

Atom	x	y	z	Atom	x	y	z
		$CI_{9H}(3)$				$CI_{9H}(4)$	
N	-1.270591889	0.452328017	-2.932487969	N	-1.255369623	0.469354776	-2.939181778
C	1.303214253	-0.159490336	-3.178873899	C	1.323319954	-0.129222005	-3.190826155
N	2.556293921	-0.467500268	-0.909709156	N	2.570838907	-0.389473999	-0.926159969
C	1.803824183	1.005718965	1.220335274	C	1.787171273	0.934940080	1.257121016
C	-1.142836860	0.792337366	1.528722520	C	-1.156797825	0.736383245	1.524426945
C	-2.338409534	0.467360891	-0.559640282	C	-2.340178084	0.430034195	-0.573145223
N	-1.696256344	-0.248972170	3.972494669	N	-1.715400062	-0.181255873	3.998316222
C	0.441909249	-0.650001859	4.975988454	C	0.411010598	-0.561800747	5.045821130
N	2.622567602	0.202344489	3.664567509	N	2.639186096	-0.074340469	3.621583649
O	2.268906459	-0.353911301	-5.205065409	O	2.283201305	-0.348219495	-5.218081514
O	-4.712912212	-0.580836699	-1.428949037	O	-4.698277609	-0.587228018	-1.502179069
H	0.677254349	-1.547521573	6.795264375	H	0.599200702	-1.319838880	6.932932878
H	-1.973044781	1.567533097	-4.295304335	H	-1.957561467	1.614179559	-4.277007764
H	4.412146535	-0.735003586	-1.183486410	H	4.399091861	-0.841131082	-1.106672251
H	4.132546475	-0.937978622	3.747793806	H	3.884893043	1.031207401	4.528190207
		$CI_{9H}(5)$					
N	-1.172890456	0.948995845	-2.790229126				
C	1.362957822	0.160562842	-3.143297674				
N	2.657501423	-0.247671514	-0.934623577				
C	1.382972616	-0.175760395	1.349839576				
C	-1.121552180	0.288549730	1.596462838				
C	-2.543276126	0.769990188	-0.684402653				
N	-1.775014746	0.383234030	4.128840617				
C	0.318544391	-0.021909704	5.327840901				
N	2.355840834	-0.357988168	3.732751753				
O	2.257398092	-0.054860342	-5.192638892				
O	-4.055356794	-1.326258897	-2.149365189				
H	0.522821678	-0.117385603	7.349763273				
H	-2.040509784	1.426648526	-4.403609841				
H	4.359603331	-1.040956989	-1.113957005				
H	4.149720049	-0.613762247	4.238960435				

Table S11: Mulliken atomic charges on the O_{10}, O_{11} and N_9 (N_7) atoms of the 7H-diketo (9H-diketo) tautomer of xanthine for the S_0 and lowest three $^1n\pi^*$ states, calculated at the CASSCF(20,14)(11π3n)/aug-cc-pVDZ level. CASPT2 vertical excitation energies of the $^1n\pi^*$ states (ΔE, in eV) are also shown.

	7H-diketo				9H-diketo			
State	ΔE	O_{10}	O_{11}	N_9	ΔE	O_{10}	O_{11}	N_7
S_0		**-0.72**	**-0.85**	**-0.83**		**-0.73**	**-0.80**	**-0.97**
$^1n\pi^*$	4.91	-0.73	**-0.47**	-0.81	4.90	-0.74	**-0.45**	-1.01
$^1n\pi^*$	6.23	**-0.33**	-0.87	-0.84	6.18	**-0.34**	-0.82	-0.98
$^1n\pi^*$	6.35	-0.73	-0.86	**-0.46**	6.45	-0.73	-0.83	**-0.74**

Table S12: CC2 vertical excitation energies of the low-lying singlet excited states of xanthine tautomers (in eV)

State	cc-pVDZ	State	cc-pVTZ	State	aug-cc-pVDZ	State	aug-cc-pVTZ
				7H-diketo			
$^1A'$ states							
$^1\pi\pi^*$	5.23	$^1\pi\pi^*$	5.12	$^1\pi\pi^*$	4.92	$^1\pi\pi^*$	4.99
$^1\pi\pi^*$	6.18	$^1\pi\pi^*$	6.11	$^1\pi\pi^*$	5.90	$^1\pi\pi^*$	5.98
$^1\pi\pi^*$	6.78	$^1\pi\pi^*$	6.66	$^1\mathrm{n}\sigma^*$	6.32	$^1\pi\pi^*$	6.44
$^1\pi\pi^*$	6.95	$^1\pi\pi^*$	6.79	$^1\pi\pi^*$	6.36	$^1\mathrm{n}\sigma^*$	6.46
$^1\pi\pi^*$	7.07	$^1\pi\pi^*$	6.94	$^1\pi\pi^*$	6.43	$^1\pi\pi^*$	6.50
$^1A''$ states							
$^1\mathrm{n}\pi^*$	5.24	$^1\mathrm{n}\pi^*$	5.17	$^1\mathrm{n}\pi^*$	5.01	$^1\mathrm{n}\pi^*$	5.06
$^1\mathrm{n}\pi^*$	6.60	$^1\mathrm{n}\pi^*$	6.52	$^1\pi\sigma^*$	5.46	$^1\pi\sigma^*$	5.62
$^1\mathrm{n}\pi^*$	6.70	$^1\mathrm{n}\pi^*$	6.59	$^1\pi\sigma^*$	5.87	$^1\pi\sigma^*$	6.04
$^1\mathrm{n}\pi^*$	6.98	$^1\mathrm{n}\pi^*$	6.84	$^1\mathrm{n}\pi^*$	6.31	$^1\mathrm{n}\pi^*$	6.37
$^1\pi\sigma^*$	7.23	$^1\pi\sigma^*$	6.88	$^1\mathrm{n}\pi^*$	6.42	$^1\mathrm{n}\pi^*$	6.45
				9H-diketo			
$^1A'$ states							
$^1\pi\pi^*$	5.66	$^1\pi\pi^*$	5.53	$^1\pi\pi^*$	5.30	$^1\pi\pi^*$	5.36
$^1\pi\pi^*$	6.14	$^1\pi\pi^*$	6.04	$^1\pi\pi^*$	5.82	$^1\pi\pi^*$	5.90
$^1\pi\pi^*$	7.08	$^1\pi\pi^*$	6.89	$^1\mathrm{n}\sigma^*$	5.97	$^1\mathrm{n}\sigma^*$	6.13
$^1\pi\pi^*$	7.11	$^1\pi\pi^*$	6.99	$^1\pi\pi^*$	6.44	$^1\pi\pi^*$	6.45
$^1\pi\pi^*$	7.68	$^1\mathrm{n}\sigma^*$	7.34	$^1\mathrm{n}\sigma^*$	6.57	$^1\pi\pi^*$	6.63
$^1A''$ states							
$^1\mathrm{n}\pi^*$	5.32	$^1\mathrm{n}\pi^*$	5.25	$^1\pi\sigma^*$	4.92	$^1\pi\sigma^*$	5.10
$^1\pi\sigma^*$	6.51	$^1\pi\sigma^*$	6.07	$^1\mathrm{n}\pi^*$	5.08	$^1\mathrm{n}\pi^*$	5.13
$^1\mathrm{n}\pi^*$	6.53	$^1\mathrm{n}\pi^*$	6.46	$^1\pi\sigma^*$	5.83	$^1\pi\sigma^*$	6.00
$^1\mathrm{n}\pi^*$	7.01	$^1\mathrm{n}\pi^*$	6.83	$^1\pi\sigma^*$	6.12	$^1\pi\sigma^*$	6.23
$^1\mathrm{n}\pi^*$	7.21	$^1\pi\sigma^*$	7.06	$^1\mathrm{n}\pi^*$	6.23	$^1\mathrm{n}\pi^*$	6.30

Table S13: ADC(2) vertical excitation energies of the low-lying singlet excited states of xanthine tautomers (in eV)

State	cc-pVDZ	State	cc-pVTZ	State	aug-cc-pVDZ	State	aug-cc-pVTZ
				7H-diketo			
$^1A'$ states							
$^1\pi\pi^*$	5.14	$^1\pi\pi^*$	5.03	$^1\pi\pi^*$	4.82	$^1\pi\pi^*$	4.90
$^1\pi\pi^*$	6.12	$^1\pi\pi^*$	6.05	$^1\pi\pi^*$	5.84	$^1\pi\pi^*$	5.93
$^1\pi\pi^*$	6.58	$^1\pi\pi^*$	6.48	$^1\pi\pi^*$	6.16	$^1\pi\pi^*$	6.27
$^1\pi\pi^*$	6.85	$^1\pi\pi^*$	6.69	$^1\mathrm{n}\sigma^*$	6.22	$^1\pi\pi^*$	6.40
$^1\pi\pi^*$	7.00	$^1\pi\pi^*$	6.87	$^1\pi\pi^*$	6.32	$^1\mathrm{n}\sigma^*$	6.44
$^1A''$ states							
$^1\mathrm{n}\pi^*$	4.98	$^1\mathrm{n}\pi^*$	4.94	$^1\mathrm{n}\pi^*$	4.75	$^1\mathrm{n}\pi^*$	4.82
$^1\mathrm{n}\pi^*$	6.33	$^1\mathrm{n}\pi^*$	6.29	$^1\pi\sigma^*$	5.47	$^1\pi\sigma^*$	5.67
$^1\mathrm{n}\pi^*$	6.60	$^1\mathrm{n}\pi^*$	6.48	$^1\pi\sigma^*$	5.88	$^1\pi\sigma^*$	6.10
$^1\mathrm{n}\pi^*$	6.85	$^1\mathrm{n}\pi^*$	6.73	$^1\mathrm{n}\pi^*$	6.02	$^1\mathrm{n}\pi^*$	6.12
$^1\pi\sigma^*$	7.32	$^1\pi\sigma^*$	6.97	$^1\mathrm{n}\pi^*$	6.33	$^1\mathrm{n}\pi^*$	6.36
				9H-diketo			
$^1A'$ states							
$^1\pi\pi^*$	5.62	$^1\pi\pi^*$	5.49	$^1\pi\pi^*$	5.26	$^1\pi\pi^*$	5.33
$^1\pi\pi^*$	6.12	$^1\pi\pi^*$	6.01	$^1\pi\pi^*$	5.78	$^1\pi\pi^*$	5.86
$^1\pi\pi^*$	6.95	$^1\pi\pi^*$	6.84	$^1\mathrm{n}\sigma^*$	5.89	$^1\mathrm{n}\sigma^*$	6.11
$^1\pi\pi^*$	7.04	$^1\pi\pi^*$	6.85	$^1\pi\pi^*$	6.40	$^1\pi\pi^*$	6.46
$^1\pi\pi^*$	7.57	$^1\mathrm{n}\sigma^*$	7.35	$^1\pi\pi^*$	6.46	$^1\pi\pi^*$	6.60
$^1A''$ states							
$^1\mathrm{n}\pi^*$	5.04	$^1\mathrm{n}\pi^*$	5.00	$^1\mathrm{n}\pi^*$	4.79	$^1\mathrm{n}\pi^*$	4.87
$^1\mathrm{n}\pi^*$	6.27	$^1\pi\sigma^*$	6.16	$^1\pi\sigma^*$	4.95	$^1\pi\sigma^*$	5.17
$^1\pi\sigma^*$	6.61	$^1\mathrm{n}\pi^*$	6.23	$^1\pi\sigma^*$	5.86	$^1\mathrm{n}\pi^*$	6.07
$^1\mathrm{n}\pi^*$	6.94	$^1\mathrm{n}\pi^*$	6.48	$^1\mathrm{n}\pi^*$	5.96	$^1\pi\sigma^*$	6.08
$^1\mathrm{n}\pi^*$	7.12	$^1\mathrm{n}\pi^*$	6.99	$^1\pi\sigma^*$	6.15	$^1\pi\sigma^*$	6.31

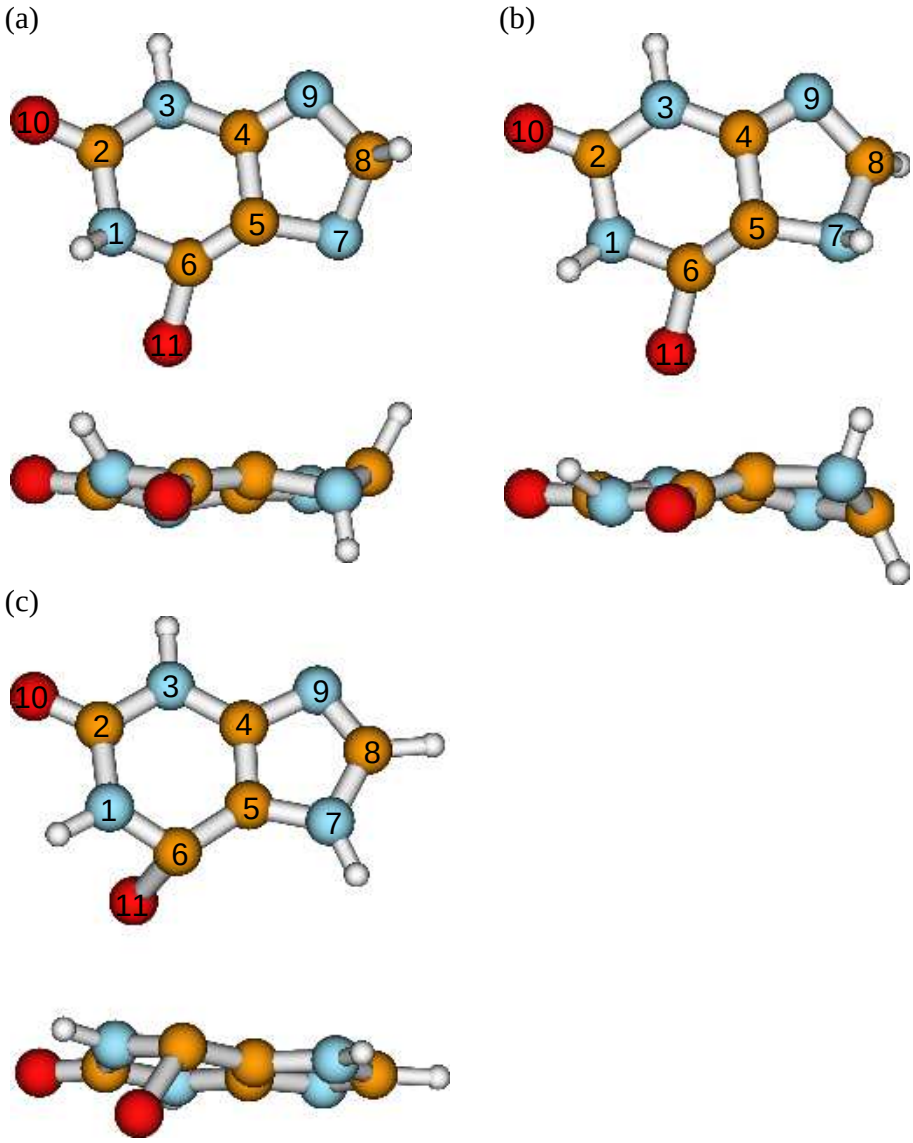

Figure S1: $^1n\pi^*$–S_0 CI geometries of the 7H-diketo tautomer of xanthine, optimized at the CASSCF(10,9/8π1n)/cc-pVDZ level: $CI_{7H}(3)$ (a), $CI_{7H}(4)$ (b) and $CI_{7H}(5)$ (c).

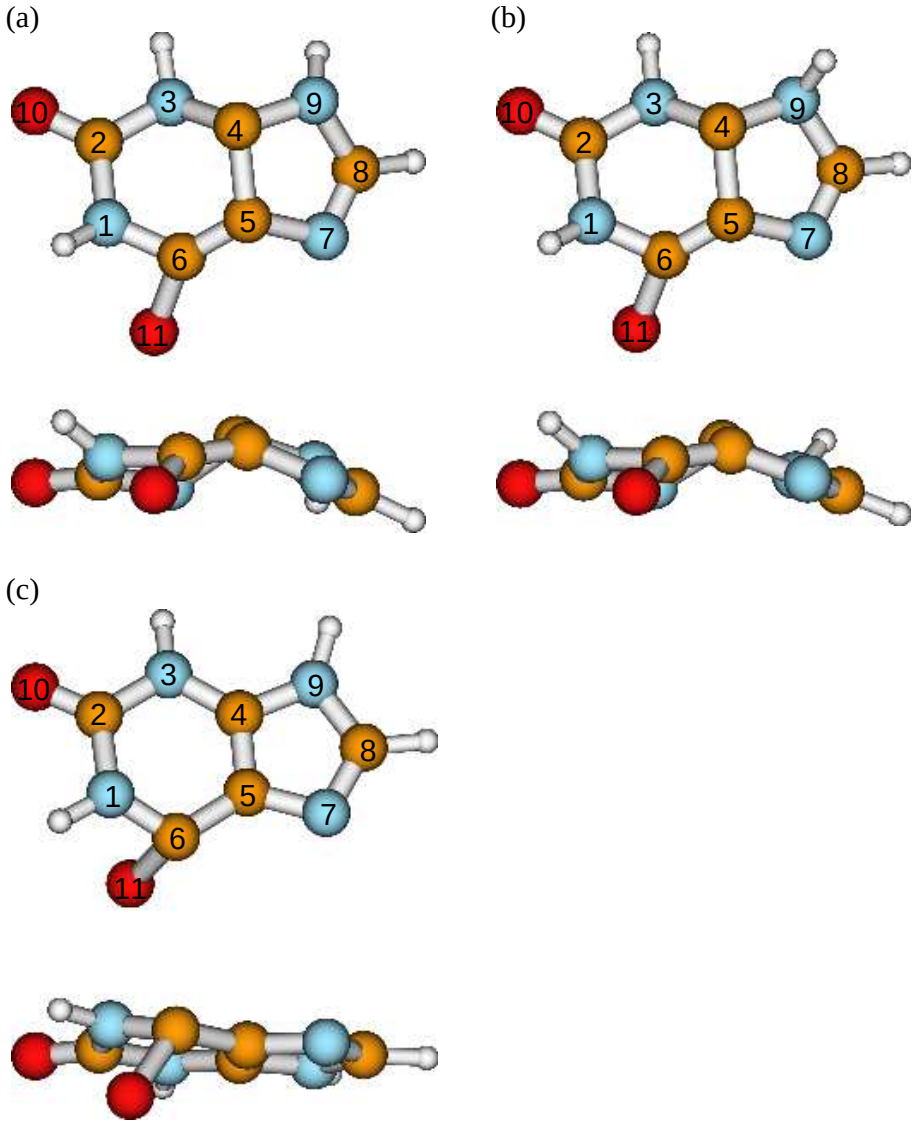

Figure S2: $^1n\pi^*$–S_0 CI geometries of the 9H-diketo tautomer of xanthine, optimized at the CASSCF(10,9/8π1n)/cc-pVDZ level: $CI_{9H}(3)$ (a), $CI_{9H}(4)$ (b) and $CI_{9H}(5)$ (c).