Supplementary Information to: "Fast and slow excited-state intramolecular proton transfer in 3-hydroxychromone: a two-state story?"

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Stationary points: Cartesian Coordinates (Å)

cis

Atoms	X	Y	Z
C	-7.602824	-2.72497	0.0
C	-4.994051	-2.796632	0.0
C	-3.586139	-0.542843	0.0
C	-4.873761	1.775936	0.0
C	-7.517935	1.860755	0.0
C	-8.859403	-0.383365	0.0
H	-8.691988	-4.475586	0.0
H	-3.946478	-4.572748	0.0
C	-0.834282	-0.55859	0.0
H	-8.456199	3.695497	0.0
H	-10.921682	-0.326341	0.0
C	-1.087851	4.053875	0.0
C	0.341322	1.934964	0.0
H	-0.333811	5.967164	0.0
O	0.526202	-2.449166	0.0
O	2.874772	1.945312	0.0
H	3.285206	0.136332	0.0
O	-3.647963	4.018508	0.0

cis*

Atoms	X	Y	Z
C	-7.634783	-2.728457	0.0
C	-4.988781	-2.863073	0.0
C	-3.529736	-0.607589	0.0
C	-4.852469	1.726582	0.0
C	-7.450663	1.867556	0.0
C	-8.877971	-0.425716	0.0
H	-8.728084	-4.479052	0.0
H	-3.995781	-4.666151	0.0
C	-0.848141	-0.555746	0.0
H	-8.360723	3.714236	0.0
H	-10.936	-0.338276	0.0
C	-1.067417	4.199	0.0
C	0.341559	2.023626	0.0
H	-0.34233	6.124325	0.0
O	0.7278	-2.317231	0.0
O	2.811451	1.886631	0.0
H	2.987512	-0.045227	0.0
O	-3.582307	4.042661	0.0

trans*

Atoms	X	Y	Z
C	-5.16769663	-1.95209789	0.0
C	-2.66248647	-2.73876646	0.0
C	-0.68186443	-0.94445101	0.0
C	-1.33309586	1.65288394	0.0
C	-3.83706419	2.42219556	0.0
C	-5.76700108	0.614262	0.0
H	-6.67299839	-3.36235407	0.0
H	-2.19383363	-4.74395851	0.0
C	1.92494067	-1.61725889	0.0
H	-4.23969814	4.44329864	0.0
H	-7.73510501	1.22725881	0.0
C	2.94563638	2.81418485	0.0
C	3.74074925	0.36138426	0.0
H	4.20706861	4.43849441	0.0
O	2.63303716	-3.99464876	0.0
O	6.2032926	-0.35072296	0.0
H	7.24929138	1.14371337	0.0
O	0.46524141	3.49281287	0.0

T*

Atoms	X	Y	Z
C	-5.09007765	-2.0673449	0.0
C	-2.54875012	-2.77971779	0.0
C	-0.63829313	-0.93197695	0.0
C	-1.34446757	1.65248435	0.0
C	-3.87124997	2.35504139	0.0
C	-5.74601836	0.47624217	0.0
H	-6.55891867	-3.51441758	0.0
H	-1.99504842	-4.76379375	0.0
C	1.99192157	-1.47388664	0.0
H	-4.34405998	4.3599017	0.0
H	-7.73098264	1.03603813	0.0
C	2.91682196	3.01019104	0.0
C	3.75810735	0.55800002	0.0
H	4.12065228	4.6723953	0.0
O	2.84534291	-3.8390346	0.0
O	6.16360324	-0.08355845	0.0
O	0.39756831	3.55468915	0.0
H	4.68827728	-3.64108879	0.0

$Min_{+/-}$

Atoms	X	Y	Z
C	-1.05867449	0.01083867	-2.7241613
C	-1.46184905	0.01096937	-1.39431098
C	-0.49999829	0.0039054	-0.35717057
C	0.87119663	-0.00540388	-0.71594925
C	1.26382842	-0.00311706	-2.0448975
C	0.29582193	0.00422397	-3.05594397
H	-1.81326769	0.01472246	-3.51291377
H	-2.52021485	0.01507545	-1.13482548
C	-0.83339091	-0.01216364	1.02540842
H	2.33102852	-0.0072265	-2.26923279
H	0.60866453	0.00424356	-4.10087833
C	1.51594548	0.01825342	1.54067507
C	0.22448224	0.00153326	1.97794243
H	2.37143367	0.05462872	2.20933007
O	-2.08574152	-0.02987893	1.43669019
O	-0.01449982	-0.01950037	3.31477899
H	-0.91305416	0.29544296	3.47357812
O	1.85414611	-0.01951116	0.22670432

TS_2*

Atoms	X	Y	Z
C	-3.738107	-0.426328	0.0
C	-1.938409	1.56873	0.0
C	0.674976	0.943708	0.0
C	2.6325	2.76342	0.0
C	5.14607	2.0041	0.0
C	5.775099	-0.555374	0.0
C	3.867249	-2.386325	0.0
C	1.354524	-1.647046	0.0
O	-0.425071	-3.503654	0.0
C	-2.911099	-2.867778	0.0
O	-6.26486	0.019462	0.0
O	-2.719369	3.939098	0.0
H	-6.549864	1.818327	0.0
H	-4.17258	-4.487295	0.0
H	4.293915	-4.402469	0.0
H	7.750326	-1.144724	0.0
H	6.635462	3.431212	0.0
H	2.140311	4.763038	0.0

TS_{ESIPT}*

Atoms	X	Y	Z
C	1.98141787	0.32679419	0.0
C	1.02689399	-0.82462861	0.0
C	-0.35362939	-0.53350073	0.0
C	-1.38854150	-1.50359228	0.0
C	-2.72914319	-1.09761798	0.0
C	-3.06542119	0.24638772	0.0
C	-2.04336279	1.23847981	0.0
C	-0.72321109	0.84089740	0.0
O	0.21853606	1.86273400	0.0
C	1.54194779	1.62258164	0.0
O	3.19469404	-0.14015895	0.0
O	1.65597459	-1.92613952	0.0
H	2.82673638	-1.23711381	0.0
H	2.15316419	2.52240876	0.0
H	-2.27766713	2.30256928	0.0
H	-4.11065145	0.55725272	0.0
H	-3.51631146	-1.85427423	0.0
H	-1.11061102	-2.55713397	0.0

CoIn

Atoms	X	Y	Z
C	-1.97587409	-0.26868207	0.0
C	-1.06037312	0.85292023	0.0
C	0.35822761	0.48488109	0.0
C	1.36071668	1.46567924	0.0
C	2.68908959	1.10735413	0.0
C	3.03864162	-0.26020039	0.0
C	2.07735469	-1.23932335	0.0
C	0.72188465	-0.86653810	0.0
O	-0.18421335	-1.85530106	0.0
C	-1.50538943	-1.53246810	0.0
O	-3.29236580	0.02928788	0.0
O	-1.48765557	2.00421263	0.0
H	-3.30652294	0.99954924	0.0
H	-2.13850259	-2.41752808	0.0
H	2.33084996	-2.30021002	0.0
H	4.09249760	-0.54709778	0.0
H	3.47010067	1.86886104	0.0
H	1.03978583	2.50909378	0.0

$TS_{\tau 1}$*

Atoms	X	Y	Z
C	0.19234653	0.01976112	1.97873730
C	-0.85879966	0.00794817	1.02209066
C	-0.50070455	0.00833243	-0.36253737
C	-1.44921680	0.00771056	-1.40941857
C	-1.03254235	-0.00298932	-2.73624748
C	0.32465982	-0.01151543	-3.05174783
C	1.28133782	-0.00984528	-2.02914705
C	0.87309288	-0.00126705	-0.70526094
O	1.85019967	-0.00586527	0.24761894
C	1.49027932	0.02460633	1.55572399
O	-0.11692580	0.07173408	3.31098921
O	-2.11698943	-0.00657734	1.38157678
H	0.09560816	-0.78562042	3.70140419
H	2.33914157	0.07643729	2.23287094
H	2.35097025	-0.01557033	-2.24150634
H	0.65003591	-0.01918822	-4.09291557
H	-1.77849588	-0.00355652	-3.53309778
H	-2.51025343	0.01671716	-1.16139101

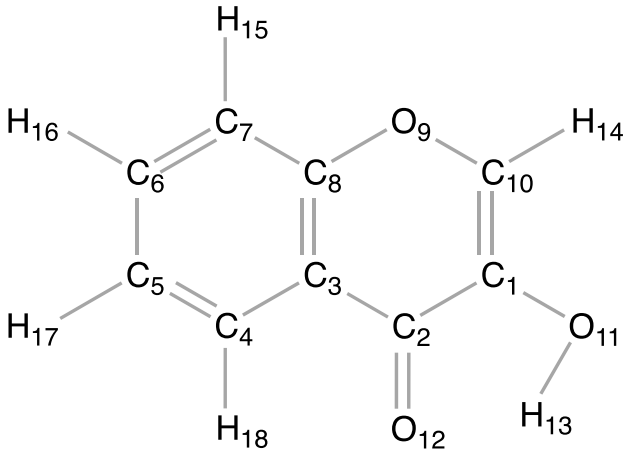
$TS_{\tau 2}$*

Atoms	X	Y	Z
C	-2.67431118	-1.06791474	0.03481459
C	-1.33110208	-1.43704282	0.05405310
C	-0.31536275	-0.46443063	0.01151916
C	-0.69981319	0.89176587	-0.01433391
C	-2.03868468	1.26213283	-0.02919963
C	-3.02846404	0.27636694	-0.01124731
H	-3.44636355	-1.83831917	0.06675008
H	-1.06826900	-2.49489353	0.12874512
C	1.07795941	-0.78044774	-0.01066142
H	-2.28428464	2.32415490	-0.05355496
H	-4.07959097	0.56861383	-0.02468504
C	1.55824470	1.56920946	0.02544008
C	2.00598770	0.27749737	0.01697500
H	2.19645853	2.44457145	0.04106113
O	1.54657809	-2.04953326	-0.03367493
O	3.29278392	-0.02753332	0.03364200
O	0.22232973	1.88383930	-0.02701450
H	0.86179239	-2.62112843	-0.40609484

Trans-T*

Atoms	X	Y	Z
C	-2.66407065	-1.08644764	0.01864363
C	-1.32065837	-1.44656814	0.02760435
C	-0.31767928	-0.46278150	0.00517050
C	-0.71145696	0.88834807	-0.00883368
C	-2.05301644	1.25248792	-0.01601745
C	-3.03089083	0.25839472	-0.00490348
H	-3.43203974	-1.86171420	0.03624334
H	-1.01741587	-2.49309354	0.06512380
C	1.07990968	-0.77759678	0.00650805
H	-2.30798900	2.31261969	-0.02854863
H	-4.08489608	0.54100752	-0.01063737
C	1.54166873	1.58129660	-0.00185211
C	1.99774854	0.28373497	0.01257756
H	2.17616846	2.45959626	0.00427611
O	1.50676422	-2.07196700	0.05644376
O	3.28658826	0.00096356	0.02777667
O	0.20824856	1.88695989	-0.01631359
H	1.52403738	-2.43127680	-0.84309617

Definition of the Z-Matrix Valence Coordinates



Atome						
C_1	**Distance**	**Atome**				
C_2	R_1	C_1	**Valence angle**	**Atome**		
C_3	R_2	C_2	θ_1	C_1	**Dihedral angle**	**Atome**
C_4	R_3	C_3	θ_2	C_2	φ_1	C_1
C_5	R_4	C_4	θ_3	C_3	φ_2	C_2
C_6	R_5	C_5	θ_4	C_4	φ_3	C_3
C_7	R_6	C_6	θ_5	C_5	φ_4	C_4
C_8	R_7	C_7	θ_6	C_6	φ_5	C_5
O_9	R_8	C_8	θ_7	C_7	φ_6	C_6
C_{10}	R_9	O_9	θ_8	C_8	φ_7	C_7
O_{11}	R_{10}	C_1	θ_9	C_2	φ_8	C_3
O_{12}	R_{11}	C_2	θ_{10}	C_1	φ_9	O_{11}
H_{13}	R_{12}	O_{11}	θ_{11}	C_1	φ_{10}	C_2
H_{14}	R_{13}	C_{10}	θ_{12}	O_9	φ_{11}	C_8
H_{15}	R_{14}	C_7	θ_{13}	C_6	φ_{12}	C_5
H_{16}	R_{15}	C_6	θ_{14}	C_7	φ_{13}	C_8
H_{17}	R_{16}	C_5	θ_{15}	C_6	φ_{14}	C_7
H_{18}	R_{17}	C_4	θ_{16}	C_5	φ_{15}	C_6

One-Dimensional Quantum Dynamics Along the Torsion Direction

The H-torsion is a symmetric (i.e., up or down) and periodic motion that should, in principle, involve periodic functions rather than quadratic expansions in the expressions of the potential-energy functions. Nevertheless, using this type of functions will complicate the formalism on which our model is based, as we should then adapt the mathematical relationships among all derivatives. In particular, implementing expressions of the quasidiabatic electronic couplings with periodic functions along this torsion coordinate would require a fitting procedure of their parameters; in addition the presence of a second-order Jahn-Teller effect at TS_2* adds a difficulty that could be tedious to recast in terms of periodic functions rather than a second-order expansion. However, if the wavepacket does not have time to tunnel through the hydrogen torsion barrier to go from the TS_2* region to the trans* minimum (i.e. 0.088 eV) — in other words, if the wavepacket does not spread significantly along the hydrogen torsion direction to form the trans* species — then an adequate periodic description of this motion and the description of the trans* region in our model will not be mandatory.

In order to check this hypothesis, we ran a one-dimensional quantum-dynamics simulation along the hydrogen-torsion. To this end, we built a one-dimensional potential-energy curve (for the first-excited state) along the hydrogen-torsion coordinate (dihedral angle denoted β) using a periodic function (i.e., a cosine function, Eq. SI.1). The corresponding parameters were optimized for the function to go trough the relevant stationary points along the hydrogen-torsion (i.e. TS_2*, $Min_{\pm}$*, $TS_{\tau 1}$*, and trans*). Note that $Min_{\pm}$* and $TS_{\tau 1}$* are not displaced only along the hydrogen-torsion from TS_2*; however, this is a good approximation (99% and 98% overlaps between the normalized directions of the actual displacements and the hydrogen-torsion coordinate). The resulting one-dimensional potential-energy curve along the hydrogen-torsion is depicted on Fig. SI-1; one can notice a slight shift between the ab-initio and the one-dimensional model at the relevant stationary points, which is expected to be too small to have a relevant impact on the wavepacket behavior (no more than about 10^{-3} eV in terms of energy).

$$E_{1D}(\beta) = 3.7429519 * 10^{-3} - 2.3153736 * 10^{-3} * \cos(\beta) - 1.6050716 * 10^{-3} * \cos(2\beta) + 1.2737786 * 10^{-3} * \cos(3\beta) \quad \text{Eq. SI.1}$$

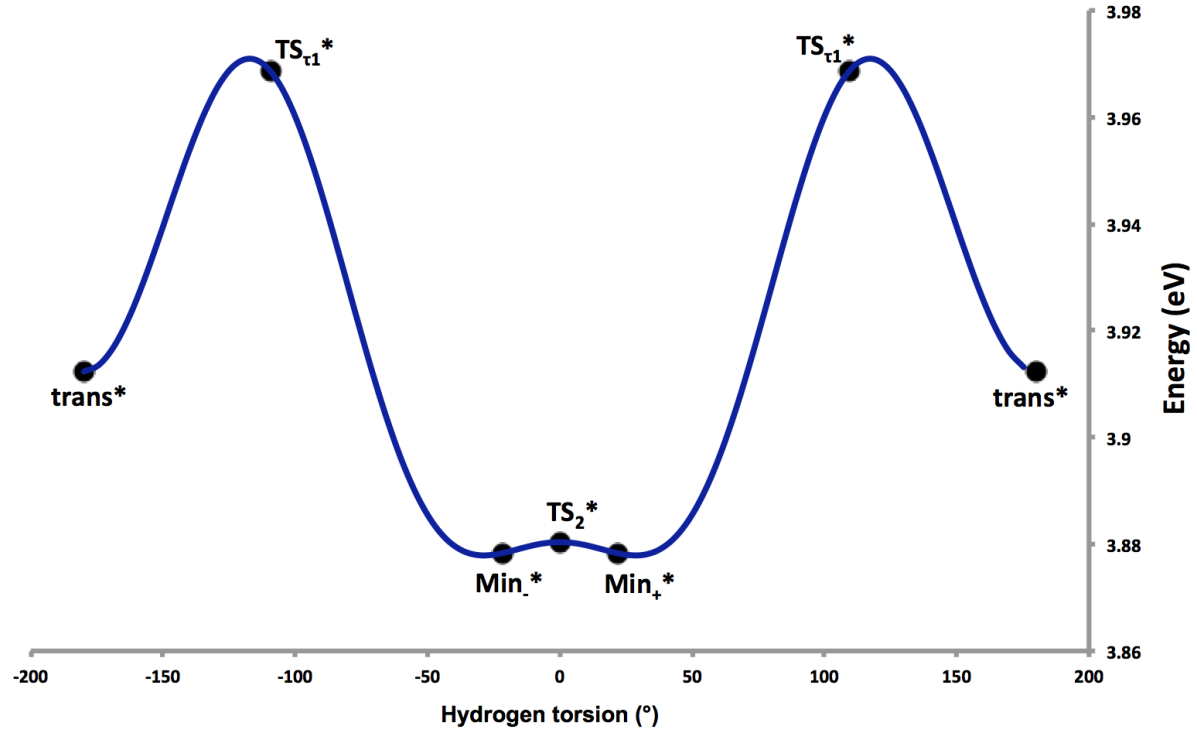


Fig. SI-1 One-dimensional potential-energy curve along the hydrogen-torsion coordinate (β).

The following one-dimensional wavepacket propagation starting at TS_2* (Fig. SI-2) was achieved using the ElVibRot program developed at the Laboratoire de Chimie Physique, Orsay, France, by David Lauvergnat.

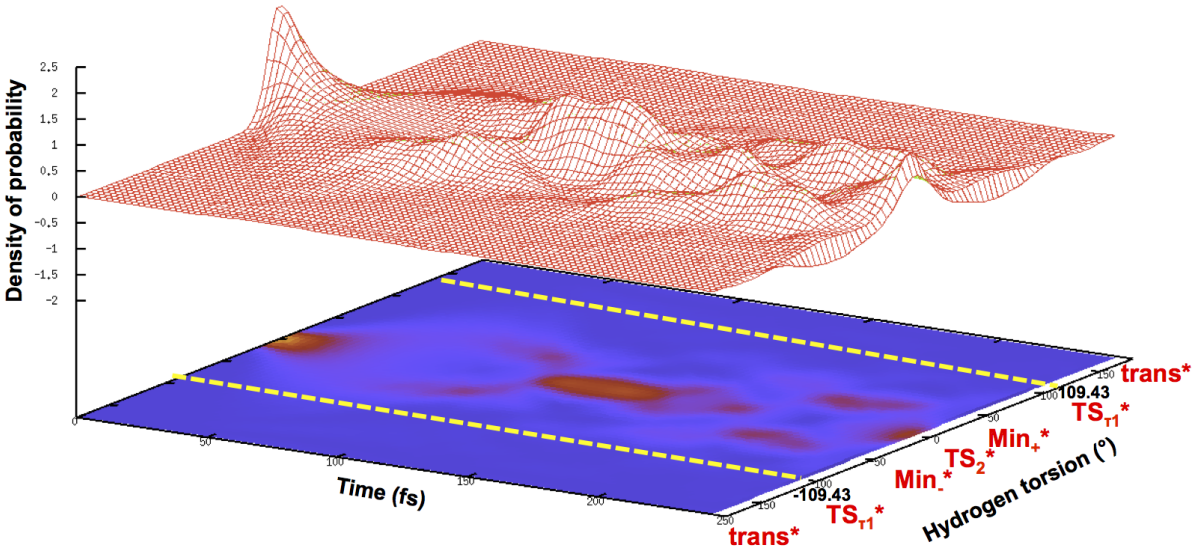


Fig. SI-2 One-dimensional wavepacket propagation along the hydrogen-torsion coordinate over time (wavepacket isodensity contour plot).

The average energy of the one-dimensional wavepacket is 0.021 eV above TS_2*, significantly below the 0.088 eV barrier. Fig. SI-2 shows the time evolution of the density of probability along the hydrogen-torsion coordinate during 250 fs. Initially (i.e., t = 0 fs) the wavepacket is centered on TS_2*, and it oscillates in time along the hydrogen-torsion coordinate ("breathing" of the wavepacket). One can notice that the density of probability stays very close to zero within the trans* region. In other words, the wavepacket does not tunnel through the torsion barrier and does not spread along the TS_2*-trans* isomerization pathway.

In conclusion, as the wavepacket stays localized within the TS_2* region, it will thus not spread significantly along the hydrogen-torsion coordinate, at least during 250 fs. This justifies why it is not necessary in a first stage to have an adequate description of the entire hydrogen-torsion motion (i.e., using periodic functions). The TS_2* region (from 0° to 20°) is thus the most relevant part of the hydrogen-torsion pathway and a quadratic expansion is sufficiently accurate within the relevant time scale for the dynamics under study. Note that this simulation brings information about the efficiency of tunneling but does not address intramolecular vibrational relaxation.

Full-Dimensional Quantum-Dynamics Computational Details

Relaxation: 20fs

ZPE: 3.665337 eV

KEO: numerical; zero-order Taylor expansion

Primitive basis: Harmonic Oscillator with 40 primitive basis functions per coordinate.

ML-tree in the "ML-MCTDH" input format:

 # Label of the layer > number of SPFs for Qi

0> 3 3

 # Electronic

1> [el]

 # Vibrational

1> 6 6 6 6

2> 6 6

3> [Q_2 Q_3]

3> 6 6 6

4> 6 6

5> [Q_4 Q_5]

5> [Q_6 Q_7]

4> 6 6

5> [Q_8 Q_9]

5> [Q_{10} Q_{11}]

4> 6 6

5> [Q_{12} Q_{13}]

5> [Q_{14} Q_{15}]

2> 6 6

3> [Q_{16} Q_{17}]

3> [Q_{18} Q_{19}]

2> 6 6 6 6

3> [Q_{20}]

3> 6 6

4> [Q_{21} Q_{22}]

4> [Q_{23} Q_{24}]

3> 6 6

4> [Q_{25} Q_{26}]

4> [Q_{27} Q_{28}]

3> 6 6

4> [Q_{29} Q_{30}]

4> [Q_{31} Q_{32}]

2> 6 6

3> [Q_1]

> 6 6 6 6

4> [Q_{33}]

4> [Q_{34} Q_{35}]

4> [Q_{36} Q_{37}]

4> [Q_{38} Q_{39}]

Geometry Deviations between the Model and ab-initio data For $Min_{+/-}$

Distances are given in bohr and angles in radian.

Z-Matrix Valence Coordinates	Model	Ab-initio	Deviation (i.e ab-initio – model)
R_1	2.687508347	2.690151	0.002642653
R_2	2.686982462	2.687686	0.000703538
θ_1	2.069451888	2.067155	-0.002296888
R_3	2.672797099	2.673021	0.000223901
θ_2	2.158254416	2.157311	-0.000943416
φ_1	3.111918836	3.126248	0.014329164
R_4	2.625919346	2.626015	9.56536E-05
θ_3	2.099446894	2.099472	2.51055E-05
φ_2	3.116581008	3.128405	0.011823992
R_5	2.635638366	2.635318	-0.000320366
θ_4	2.105347504	2.105365	1.74962E-05
φ_3	-0.002932004	2.44E-04	0.003176004
R_6	2.644632196	2.645141	0.000508804
θ_5	2.094288978	2.094259	-2.9978E-05
φ_4	6.280871686	6.283185307	0.002313621
R_7	2.619058029	2.618671	-0.000387029
θ_6	2.090617146	2.090675	5.78537E-05
φ_5	-0.00112043	0	0.00112043
R_8	2.572205126	2.57366	0.001454874
θ_7	2.048271267	2.048006	-0.000265267
φ_6	3.158756542	3.147108	-0.011648542
R_9	2.565658317	2.56505	-0.000608317
θ_8	2.084663789	2.08286	-0.001803789
φ_7	3.215661799	3.175393	-0.040268799
R_{10}	2.56527021	2.566593	0.00132279
θ_9	2.128871215	2.126603	-0.002268215
φ_8	3.155214529	3.135375	-0.019839529
R_{11}	2.494466621	2.491225	-0.003241621
θ_{10}	2.088378063	2.091177	0.002798937
φ_9	6.267467815	6.283185307	0.015717492
R_{12}	1.821144993	1.824121	0.002976007
θ_{11}	1.901620468	1.897255	-0.004365468
φ_{10}	0.377949	0.38	0.002051
R_{13}	2.052889832	2.053	0.000110168
θ_{12}	1.982319537	1.982806	0.000486463
φ_{11}	3.044821436	3.090383	0.045561564

R_{14}	2.060797876	2.060806	8.12395E-06
θ_{13}	2.127106154	2.127256	0.000149846
φ_{12}	3.14347856	3.140297	-0.00318156
R_{15}	2.061235664	2.061241	5.33591E-06
θ_{14}	2.08697448	2.087029	5.45201E-05
φ_{13}	3.138054884	3.139745	0.001690116
R_{16}	2.062754434	2.062791	3.65659E-05
θ_{15}	2.093823387	2.093857	3.36133E-05
φ_{14}	3.136253124	3.139659	0.003405876
R_{17}	2.059299413	2.059273	-2.64128E-05
θ_{16}	2.105524509	2.105595	7.04909E-05
φ_{15}	3.139007975	3.140389	0.001381025

Geometry Deviations between the Model and ab-initio data For CoIn

Distances are given in bohr and angles in radian.

Z-Matrix Valence Coordinates	Model	Ab-initio	Deviation (i.e ab-initio – model)
R_1	2.756884	2.740141	-0.016743
R_2	2.75206	2.766031	0.013971
θ_1	2.005688	2.002355	-0.003333
R_3	2.657523	2.65174	-0.005783
θ_2	2.115333	2.123512	-0.008179
φ_1	3.141593	3.141606	-1.3E-05
R_4	2.601964	2.609898	-0.007934
θ_3	2.103277	2.101771	0.001506
φ_2	3.141593	3.141585	8E-06
R_5	2.665405	2.657454	0.007951
θ_4	2.090758	2.085768	-0.00499
φ_3	0.000039	0	-0.000039
R_6	2.597296	2.597296	0
θ_5	2.110259	2.114163	0.003904
φ_4	0.000039	0	-0.000039
R_7	2.645689	2.654405	0.008716
θ_6	2.077566	2.078406	0.00084
φ_5	0.000063	0	-0.000063
R_8	2.555814	2.538676	-0.017138
θ_7	2.039025	2.043171	0.004146
φ_6	3.141499	3.141593	9.4E-05
R_9	2.560499	2.568216	0.007717
θ_8	2.084903	2.075318	-0.009585
φ_7	3.141516	3.141593	7.7E-05

R_{10}	2.533607	2.547229	0.013622
θ_9	2.015487	2.029314	0.013827
φ_8	3.141483	3.141593	0.00011
R_{11}	2.329205	2.32234	-0.006865
θ_{10}	2.077228	2.096765	0.019537
φ_9	3.141516	3.141593	7.7E-05
R_{12}	1.854963	1.837967	-0.016996
θ_{11}	1.789796	1.804335	0.014539
φ_{10}	3.141483	3.141593	0.00011
R_{13}	2.056587	2.056419	-0.000168
θ_{12}	1.960087	1.953674	-0.006413
φ_{11}	3.141615	3.141593	-2.2E-05
R_{14}	2.060728	2.061124	0.000396
θ_{13}	2.130062	2.130683	0.000621
φ_{12}	3.141589	3.141593	4E-06
R_{15}	2.0632	2.063827	0.000627
θ_{14}	2.081982	2.081364	-0.000618
φ_{13}	3.141639	3.141593	-4.6E-05
R_{16}	2.06188	2.061446	-0.000434
θ_{15}	2.092482	2.093139	0.000657
φ_{14}	3.141579	3.141593	1.4E-05
R_{17}	2.062037	2.062749	0.000712
θ_{16}	2.131132	2.132361	0.001229
φ_{15}	3.141573	3.141593	2E-05

CC2, ADC(2), and EOM-CCSD Results

Energies relative to S_0 cis in eV. Basis set: cc-pVTZ. Geometries optimized at the TD-PBEO/cc-pVTZ level of theory.

		TS_2*	cis	cis*
TD-PBE0	S_0	0.39	0	0.32
	S_1	3.88	4.11	3.83
	S_2	4.39	4.23	4.62
CC2	S_0	0.25	0	0.31
	S_1	3.71	4.20	3.85
	S_2	5.35	4.30	4.65
ADC(2)	S_0	0.33	0	0.38
	S_1	3.45	4.09	3.74
	S_2	4.22	4.09	4.47
EOM-CCSD	S_0	0.39	0	0.44
	S_1	4.18	4.52	4.41
	S_2	4.74	4.52	5.04

EOM-CCSD calculations were performed with the Molpro 2010.1 package.

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