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

Supplementary information for:

A three-state model for Photo-Fries rearrangement

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SI1 – Molecular orbitals

The active space for phenyl acetate is shown in Figure S1 and is composed of seven occupied and five virtual orbitals: 4 π and 4 π*, 1 orbital pair σ/σ* of the OC—O bond, and two non-bonded electrons pairs, one in the oxygen of the carbonyl group and another one in the oxygen bonded to the phenyl ring. The active space for the remaining molecules included the same orbitals described for PA.

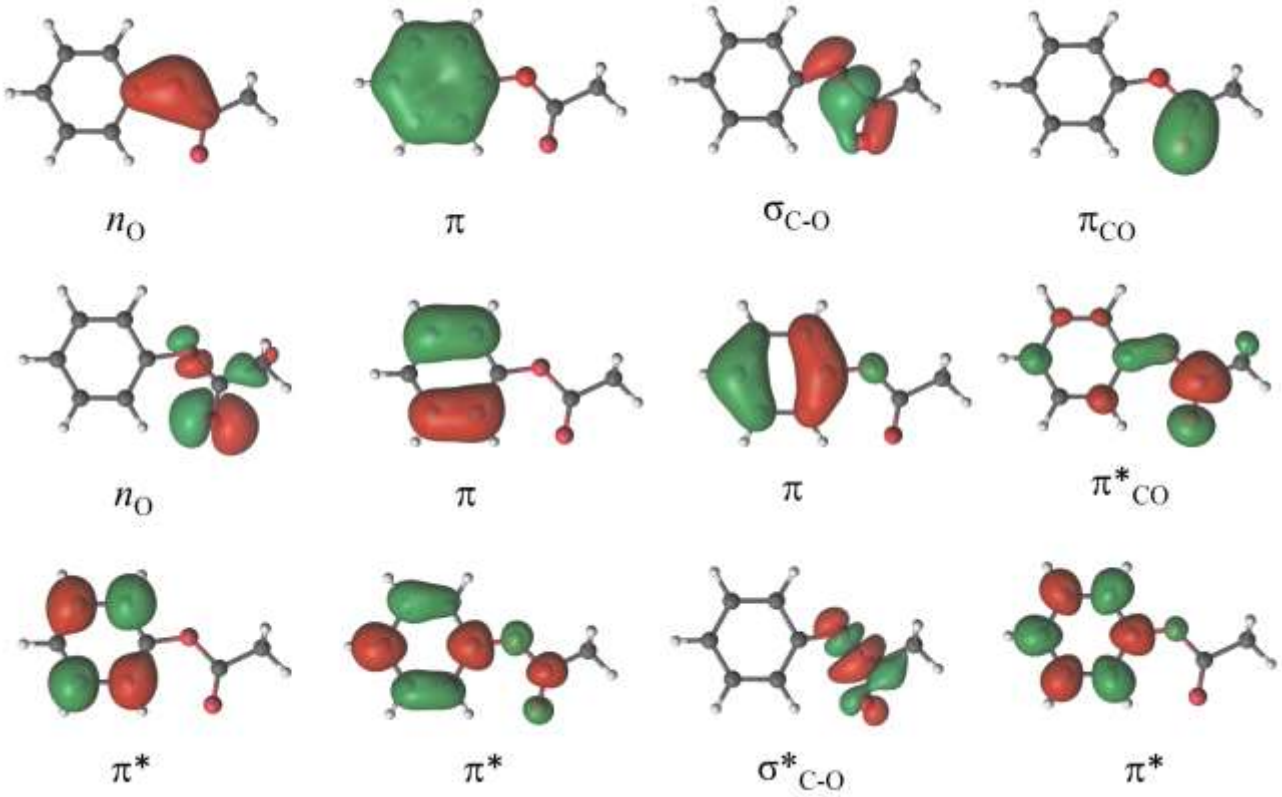

Figure S1. Active space chosen at the ground state of phenyl acetate.

SI2 – ABSORPTION SPECTRUM

Figure S2 shows the absorption spectrum obtained experimentally in cyclohexane[1] and the theoretical spectrum calculated with MS-CASPT2.

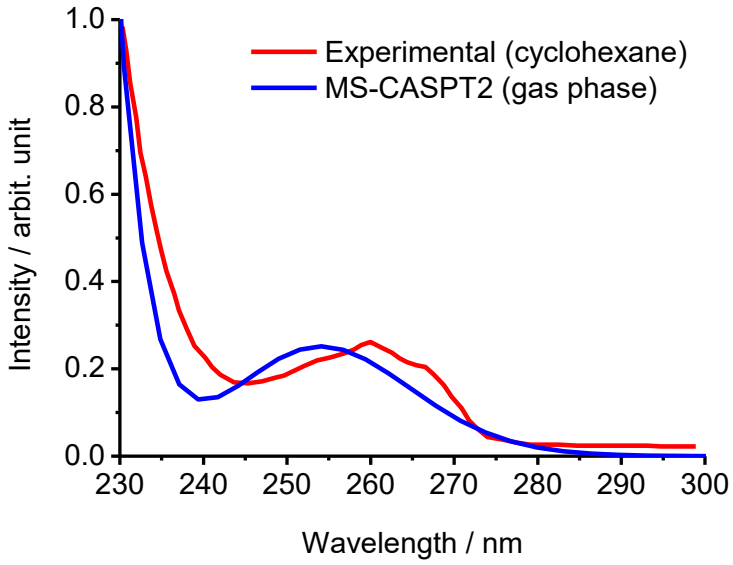

Figure S2. Absorption spectra of phenyl acetate. On the left: experimental results in cyclohexane from Harris *et al*.[1] On the right: theoretical MS-CASPT2 results averaged over 7 states, convoluted with normalized Gaussian functions.

1 S. J. Harris, D. Murdock, M.P. Grubb, G. M. Greetham, I. P. Clark, M. Towrie, M. N. Ashfold, *Chem. Sci.* **2014**, *5*, 707.

SI3 – PL TO PYR ENERGY PROFILE

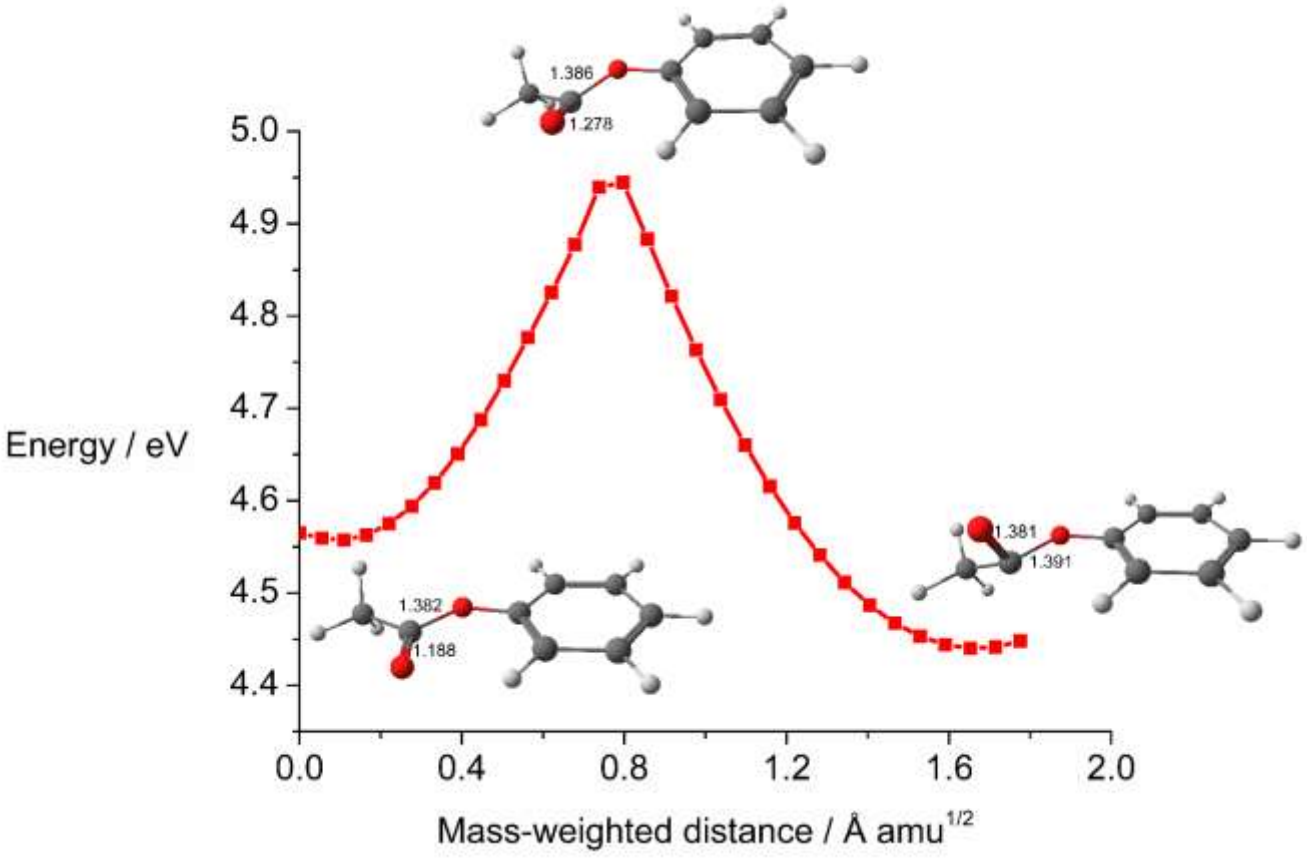

Figure S3. LIIC energy profile between the S_1-PL minimum and S_1-PYR minimum calculated with the MS-CASPT2//CASSCF protocol.

SI4 – Energies of the stationary points and conical intersection

Table S1. Energies of the stationary points of Phenyl acetate (a.u.).

Phenyl acetate	CASSCF	CASPT2
Ground state	-457.555262	-458.824853
S_1-Planar (ππ* state)	-457.381979	-458.657088
S_1-Pyramidal (nπ* state)	-457.395591	-458.661538
Conical intersection	-457.423657	-458.698828
Radical complex	-457.464280	-458.710285
Cyclohexadienone intermediate	-457.521471	-458.790990
Transition state	-457.408856	-458.715260
ortho-hydroxyacetophenone – after tunneling	-457.518348	-458.821898
ortho-hydroxyacetophenone – Global minimum	-457.553133	-458.835350

Table S2. Energies of planar and pyramidal minima of the four molecules.

	CASSCF			MS-CASPT2		
Molecule	^{1}ππ* (a.u.)	^{1}nπ* (a.u.)	Δ*E* (eV)	^{1}ππ* (a.u.)	^{1}nπ* (a.u.)	Δ*E* (eV)
a Phenyl acetate	-457.381979	-457.395591	-0.37	-458.657088	-458.661538	-0.12
b Phenyl carbamate	-473.393516	-473.393103	0.01	-474.693310	-474.684880	0.23
c Ortho-methoxyphenyl carbamate	-587.296886	-587.294840	0.06	-588.930492	-588.915646	0.40
d Propoxur	-704.425881	-704.424778	0.03	-706.492595	-706.477245	0.42

SI5 – CARTESIAN COORDINATES

Table S3. Cartesian coordinates of species involved in Photo-Fries reaction starting from phenyl acetate optimized at SA3-CASSCF(14,12)/ANO-S-VDZP level of theory.

Phenyl acetate – Ground state

C	-1.086270290	0.579917860	4.258752840
C	-1.957435720	0.238443190	3.222523790
C	-3.236167780	-0.265138430	3.500231750
C	-3.649523460	-0.429538990	4.820759390
C	-2.788088260	-0.091921870	5.874035310
C	-1.518784080	0.407970430	5.583754480
O	-1.702308810	0.340675650	1.874323490
C	-0.536169880	0.799870010	1.300965960
O	0.424569300	1.176687690	1.890339040
C	-0.673938350	0.747827970	-0.199196330
H	-0.107009600	0.965545330	4.057274840
H	-0.845356570	0.671930660	6.387299470
H	-3.104228910	-0.217680250	6.899751380
H	-4.637050210	-0.818429030	5.026377160
H	-3.885633180	-0.519633050	2.675646230
H	-0.871079830	-0.275526760	-0.512291040
H	-1.515513950	1.363711840	-0.509977000
H	0.241748570	1.108454740	-0.656255770

Phenyl acetate – S_1-Planar ($\pi\pi^*$ state)

C	-1.047145720	0.595290680	4.267691690
C	-1.948732060	0.241813880	3.206117460
C	-3.258685710	-0.274022480	3.473499280
C	-3.690612100	-0.445728880	4.832519390
C	-2.804271570	-0.098281150	5.905066240
C	-1.494944130	0.417352120	5.620605660
O	-1.692045840	0.344630030	1.866551670
C	-0.526152560	0.803739880	1.284753420
O	0.436767900	1.181376820	1.869050500
C	-0.673912140	0.747908460	-0.214146480
H	-0.070244530	0.979988550	4.061731420
H	-0.831948990	0.677242780	6.430852040
H	-3.121078530	-0.224256490	6.929001450
H	-4.675250020	-0.833487710	5.040206350
H	-3.898933640	-0.524919760	2.643636980
H	-0.872870540	-0.276109610	-0.523908580
H	-1.517224690	1.363168810	-0.521436630
H	0.239040830	1.107462060	-0.677475860

Phenyl acetate – S_1-Pyramidal ($n\pi^*$ state)

C	-1.137498680	0.565211600	4.105263000
C	-2.033656220	0.095160870	3.145662050
C	-3.281045710	-0.415744320	3.520744360
C	-3.634920630	-0.451585140	4.869779380
C	-2.747259670	0.019190090	5.846947890
C	-1.505207620	0.524302850	5.457984200
O	-1.789799940	0.092341790	1.798291010
C	-0.579638260	0.578574150	1.315958530
O	0.445057690	-0.286317560	1.647286600
C	-0.625591390	0.907252060	-0.145030850
H	-0.174442190	0.952771210	3.818737650
H	-0.810993200	0.889752350	6.201802520
H	-3.020962560	-0.009749350	6.891882690
H	-4.599897390	-0.845564020	5.156779430
H	-3.952922980	-0.773405710	2.754238820
H	-0.892621470	0.020609870	-0.723323260
H	-1.368122330	1.683642380	-0.314147710
H	0.346968500	1.267517870	-0.476339310

Conical intersection

C	-1.317770890	0.554453380	4.110383990
C	-2.256173660	0.155620670	3.089968520
C	-3.550439540	-0.388381210	3.488736970
C	-3.882534310	-0.490187960	4.827400080
C	-2.929306500	-0.065718380	5.826794000
C	-1.658935450	0.452309770	5.444288900
O	-2.013192850	0.258426990	1.828039040
C	0.081843790	0.699581210	1.321872580
O	0.752320820	-0.178130250	1.828754220
C	-0.264359180	0.877208370	-0.152714240
H	-0.333189900	0.941453630	3.793344370
H	-0.948197610	0.761377720	6.234591130
H	-3.203219510	-0.150530580	6.885669260
H	-4.847000570	-0.883202170	5.117646140
H	-4.238595040	-0.694719800	2.710018470
H	-0.408541730	-0.114806540	-0.618393540
H	-1.162294900	1.504652850	-0.272611620
H	0.623526780	1.385361340	-0.573191820

Radical complex

C	-1.445777160	-1.236214200	4.125131860
C	-2.401507770	-1.230972710	3.024998170
C	-3.565238770	-0.363284060	3.154270870
C	-3.757097760	0.389525970	4.295283860
C	-2.821025020	0.342546590	5.355683680
C	-1.667746000	-0.471040270	5.252437960
O	-2.229845890	-1.927436520	2.023990280
C	-0.766375330	1.566012750	1.996908780
O	-0.499407540	2.631746190	2.422951020
C	-0.419298050	0.968931870	0.655080950
H	-0.574672450	-1.867845070	4.026236060
H	-0.954345800	-0.487536690	6.064747430
H	-2.981717320	0.938304240	6.242112650

Cyclohexadienone intermediate

C	-1.399678950	-0.313783990	3.195412140
C	-2.768022840	-0.645021090	2.601091750
C	-3.973734230	-0.252551190	3.358611840
C	-3.879919210	0.158661090	4.643060770
C	-2.579092840	0.260172060	5.321837000
C	-1.430867380	0.020857380	4.661176030
O	-2.857329360	-1.199997090	1.530190540
C	-0.797410360	0.901954820	2.364930650
O	-0.887209540	2.027470540	2.766206270
C	-0.117596720	0.542454230	1.064677800
H	-0.753939710	-1.171079320	3.010443130
H	-0.478989100	0.121857320	5.164352770
H	-2.563099270	0.531304800	6.368000470

H	-4.627418510	1.025179170	4.382266660
H	-4.268581440	-0.346499150	2.334154570
H	0.164783290	1.671371470	0.061264950
H	0.138003750	0.048456020	0.814069570
H	-1.341204830	0.709122400	0.139162550

Transition state

i 2552.20 cm^{-1}

C	0.215750670	-0.236531820	-0.437629240
C	-0.520977250	0.982963080	-0.224953480
C	-1.775323090	1.004073120	0.458847860
C	-2.436008490	-0.198448130	0.531514000
C	-1.856884480	-1.425364550	0.041800400
C	-0.569025110	-1.458075170	-0.420424020
O	-0.001636680	1.956520120	-0.849619060
C	1.631108330	-0.374403740	0.087031940
O	2.210992750	-1.417682130	-0.069680030
C	2.295999960	0.778133830	0.816546690
H	0.663041630	0.860938020	-1.361773920
H	-0.093010770	-2.389073150	-0.685333020
H	-2.440291600	-2.332811390	0.095976840
H	-3.439439790	-0.224264470	0.934731820
H	-2.234421980	1.940479880	0.740316680
H	3.267124670	0.437065090	1.161713990
H	2.421701700	1.640989690	0.167995780
H	1.689161540	1.086585730	1.667112740

***ortho*-hydroxyacetophenone – Global minimum**

C	6.606689070	3.997704910	-0.001864520
C	6.918445110	4.604782380	1.232280770
C	7.628471150	5.824297680	1.214472190
C	8.018078270	6.425340920	0.023352500
C	7.698312300	5.805399180	-1.194523760
C	6.999593430	4.603700190	-1.204999980
H	7.876296800	6.304036510	2.146053640
H	8.560769930	7.359152500	0.038936810
H	7.994257850	6.260172670	-2.129647940
H	6.744521050	4.111725530	-2.132485690
O	5.927416700	2.823611460	-0.113736030
H	5.716675750	2.511791170	0.761245830
C	6.512006670	3.980330420	2.519339190
O	5.900635920	2.930528800	2.539051340
C	6.858360810	4.651381740	3.831937640
H	7.936988920	4.757868440	3.935885410
H	6.413822220	5.643938240	3.884839060
H	6.474331470	4.037813350	4.640533200
H	-4.773955520	0.408203680	5.198266130
H	-4.922723780	-0.365079140	2.853708160
H	0.134807570	1.448002130	0.520193500
H	0.792544250	-0.018173400	1.282685870
H	-0.762255580	-0.094884840	0.465907020

***ortho*-hydroxyacetophenone – after tunneling**

C	-1.59415205	0.13612238	3.21977210
C	-2.77375313	-0.37652641	2.65269656
C	-3.92915866	-0.53204173	3.43640289
C	-3.92939416	-0.18425779	4.78090383
C	-2.76126158	0.32938543	5.36774000
C	-1.62140645	0.48206717	4.59207829
O	-2.92966094	-0.75940475	1.36014482
C	-0.24356146	0.37327407	2.51249299
O	0.68525256	0.81458111	3.13802166
C	-0.05677397	0.06343845	1.03966308
H	-2.14689372	-0.65523239	0.85316268
H	-0.71765358	0.87482393	5.02798529
H	-2.74709195	0.60398922	6.41261926
H	-4.82811290	-0.31094245	5.36815071
H	-4.81293047	-0.92974723	2.95918121
H	0.96145256	0.31672028	0.76326619
H	-0.21592455	-0.99708605	0.84134990
H	-0.74016547	0.65214782	0.42698295

Table S4. Cartesian coordinates for S0 and S1 planar and pyramidalyzed for phenyl carbamate, ortho-methoxyphenyl carbamate and Propoxur optimized at SA3-CASSCF(14,12)/ANO-S-VDZP level of theory.

Phenyl carbamate – S_0

N	-3.28609882	0.47914419	-0.18654293
C	-2.04271140	0.08820778	0.25884076
O	-1.80701416	-0.42253346	1.30191765
O	-1.10165470	0.42706744	-0.68936922
C	0.22366098	0.19016528	-0.37498776
C	0.98290267	1.22870661	0.15821444
C	2.33864689	1.00939545	0.42781727
C	2.91605870	-0.23787658	0.16497822
C	2.13573764	-1.27010962	-0.36969700
C	0.78039246	-1.05849625	-0.64332644
H	0.16266527	-1.84367885	-1.05350447
H	2.57826338	-2.23486922	-0.57424948
H	3.96340423	-0.40416030	0.37402485
H	2.93791760	1.80906491	0.83993896
H	-3.37323067	0.56609051	-1.17952749
H	0.51858068	2.18389429	0.35500227
H	-4.04260075	0.00124384	0.26202735

Phenyl carbamate –S1- Planar (ππ* state)

N	-3.31909515	0.44212806	-0.16849739
C	-2.09088428	-0.05259910	0.20942051
O	-1.89536749	-0.84775976	1.06580123
O	-1.11257325	0.56323812	-0.54522410
C	0.20199904	0.26078976	-0.28195191
C	1.04121031	1.33845292	0.14277449
C	2.43869911	1.08549259	0.35444782
C	2.96839877	-0.23330972	0.13838182
C	2.10932068	-1.30018730	-0.29738863
C	0.71181856	-1.05346774	-0.52279576
H	0.04852434	-1.84148685	-0.83620415
H	2.51205746	-2.28739014	-0.45960699
H	4.01750629	-0.42360620	0.30407258
H	3.08614254	1.88292251	0.68324911
H	-3.36026324	0.81467603	-1.09616960
H	0.61261334	2.31496274	0.29990355
H	-4.08518800	-0.15159994	0.08134341

Phenyl Carbamate – S_1-Pyramidal (nπ* state)

N	-3.33514901	0.42333044	-0.02292888
C	-2.07595344	-0.13498062	0.21648910
O	-1.99828549	-0.81908131	1.42237924
O	-1.06765122	0.80706888	0.13417216
C	0.23899485	0.40012694	0.10240515
C	1.18188009	1.43054960	0.18246961
C	2.54232752	1.12469220	0.13885510
C	2.96510665	-0.20591801	0.01817988
C	2.01257074	-1.22365739	-0.06159673
C	0.64227912	-0.92897222	-0.02163582
H	-0.08280591	-1.72326899	-0.08594870
H	2.32559483	-2.25392180	-0.15754958
H	4.01896048	-0.44248219	-0.01377279
H	3.26943023	1.92238004	0.19978302
H	-4.01674350	-0.28374487	-0.23348558
H	0.83738939	2.45027048	0.27346325
H	-3.65549141	0.98617189	0.75084259

***o*-methoxyphenyl carbamate – S_0**

N	-3.35120868	-0.34823824	-0.31363849
C	-2.09773298	-0.40276159	0.25466883
O	-1.84085408	-0.19523161	1.39241721
O	-1.17607502	-0.71473901	-0.72281047
C	0.15174435	-0.65847438	-0.36817344
C	0.77719246	0.59053855	-0.22262790
C	2.13565510	0.62600558	0.09480594
C	2.85363666	-0.56940164	0.25671177
C	2.22346159	-1.80258674	0.10268468
C	0.85729678	-1.84218662	-0.20966710
H	0.33561267	-2.78025669	-0.33021734
H	2.77718601	-2.72188752	0.22580087
H	3.90553334	-0.52289474	0.50067449
H	2.64148804	1.56877082	0.21374622
H	-3.44990620	-0.85780969	-1.16899641
H	-4.09450568	-0.48161292	0.34316323
O	-0.00342847	1.67072863	-0.42126389
C	0.47802213	2.94049076	-0.06958017
H	0.78761882	2.96627369	0.97523236
H	1.31162023	3.23886593	-0.70601178
H	-0.34944106	3.62643144	-0.21834762

***o*-methoxyphenyl carbamate – S1- Planar (ππ* state)**

N	-3.28974787	-0.20235202	-0.34208987
C	-2.02665561	-0.18097042	0.20228638
O	-1.73440376	0.26634157	1.26100108
O	-1.14097284	-0.73948971	-0.69400348
C	0.19296252	-0.67609826	-0.39073241
C	0.88258991	0.58105775	-0.42288215
C	2.29581584	0.61877261	-0.16922514
C	2.99002366	-0.59987356	0.14143733
C	2.28454168	-1.85133419	0.17631445
C	0.87720630	-1.89676599	-0.09698279
H	0.32585303	-2.82224740	-0.07457347
H	2.81492332	-2.76129358	0.40956233
H	4.05077737	-0.57645583	0.33591254

***o*-methoxyphenyl carbamate – S_1-Pyramidal (nπ* state)**

N	-0.09166765	-0.09912170	0.07590385
C	1.30429066	-0.04505292	0.01020734
O	1.91951263	-0.20740294	1.24830532
O	1.82435512	-0.95270763	-0.89684118
C	3.17272675	-0.86578351	-1.15009024
C	3.67659684	0.18501472	-1.93958299
C	5.04292068	0.21349449	-2.22608893
C	5.88911805	-0.79649476	-1.74217321
C	5.37960285	-1.83802014	-0.97009462
C	4.00968415	-1.86690620	-0.67421150
H	3.58053719	-2.65894907	-0.07862199
H	6.02981421	-2.61697908	-0.59941873
H	6.94331484	-0.75760554	-1.97744384

H	2.82838535	1.55125705	-0.24013968
H	-3.42969676	-0.87790651	-1.06662576
H	-4.02271386	-0.15182985	0.33734702
O	0.18766550	1.67632492	-0.78873030
C	0.20403242	2.77687246	0.09743723
H	-0.11414669	2.46888149	1.09079131
H	1.19445073	3.22658391	0.14873238
H	-0.49797427	3.50054953	-0.30626600

Propoxur – S0-Planar

C	-3.98731057	-0.82611717	0.30556742
N	-2.81391434	-1.34456715	-0.36687922
C	-1.58656990	-1.13458241	0.20203279
O	-1.38095246	-0.79547335	1.32104076
O	-0.60956306	-1.42423130	-0.72593735
C	0.69290557	-1.16833044	-0.36728138
C	1.16271438	0.15341191	-0.35801810
C	2.50980001	0.37959998	-0.06278672
C	3.36078647	-0.69572621	0.22692037
C	2.88007399	-2.00563045	0.21388283
C	1.53309567	-2.23907679	-0.08746677
H	1.12563559	-3.23922599	-0.10772563
H	3.53750800	-2.83406172	0.43417784
H	4.39886286	-0.49991503	0.45579585
H	2.90250727	1.38211550	-0.05336522
O	0.26989176	1.11181169	-0.69322946
C	0.38602717	2.43397451	-0.18945421
C	-0.64142180	3.25327420	-0.95435054
H	-0.45349065	3.19074401	-2.02493702
H	-1.64352333	2.87761298	-0.75474643
H	-0.59173918	4.29738378	-0.64691357
C	0.16083904	2.47719711	1.31735904
H	0.88728456	1.86486889	1.84505404
H	0.25294190	3.50403723	1.67198614
H	-0.83180442	2.10519496	1.55829837
H	1.37761882	2.81988359	-0.42482594
H	-2.80690775	-1.29232484	-1.36453835
H	-4.86864431	-1.15132661	-0.24277914
H	-4.03614886	-1.22868636	1.31330314
H	-3.98727139	0.26394547	0.36740446

Propoxur – S_1-Pyramidal (nπ* state)

C	-3.42323531	-0.29073342	-0.36525171
N	-2.94739131	-1.55838544	0.16706152
C	-1.58968984	-1.60643518	0.46206100
O	-1.29727781	-2.74062970	1.19606572
O	-0.72235153	-1.53729485	-0.63207684
C	0.58827423	-1.23002553	-0.35136629
C	0.96848694	0.11560196	-0.19312410
C	2.31688514	0.40338079	0.03777039
C	3.26336804	-0.62998347	0.09977742
C	2.87737042	-1.95834865	-0.06895817
C	1.52758557	-2.25347011	-0.29759705
H	1.19123996	-3.27045394	-0.43388212
H	3.60680790	-2.75387920	-0.02456592
H	4.30006620	-0.38243680	0.27942013
H	2.64435360	1.41872255	0.17335334
O	-0.02177634	1.02772577	-0.30337776
C	0.19549142	2.39976509	-0.02478040
C	-0.92590832	3.15401417	-0.72238640
H	5.45569254	1.00574615	-2.82636460
H	-0.42086136	-0.90126707	0.59095787
H	-0.47337764	0.74079415	0.47214651
O	2.77950690	1.09877773	-2.36041206
C	3.19987994	2.14405524	-3.19453748
H	3.92958969	2.78152230	-2.69419668
H	3.62586106	1.76278448	-4.12308984
H	2.31044752	2.72384833	-3.41832901

Propoxur – S1- Planar (ππ* state)

C	-3.99845578	-0.81697551	0.32165849
N	-2.82618061	-1.33689944	-0.35153470
C	-1.59750813	-1.12570554	0.21260620
O	-1.38679792	-0.78267148	1.32937915
O	-0.62214430	-1.41721416	-0.71962911
C	0.67803740	-1.17208035	-0.36853822
C	1.17055352	0.17511881	-0.36243945
C	2.56141772	0.41703445	-0.09022810
C	3.41915758	-0.69327199	0.21504839
C	2.90783543	-2.03562505	0.21966430
C	1.52948322	-2.28502194	-0.08191524
H	1.11950108	-3.28132684	-0.08467283
H	3.56540001	-2.85944973	0.44964057
H	4.46081909	-0.51591209	0.43224736
H	2.95935593	1.41475379	-0.10734541
O	0.29371736	1.13132946	-0.72395068
C	0.37957226	2.44381642	-0.18425347
C	-0.62693879	3.27341233	-0.96516466
H	-0.40259474	3.23668354	-2.02992330
H	-1.63272955	2.88733005	-0.80822677
H	-0.59481808	4.31051625	-0.63272259
C	0.10500751	2.44874287	1.31446653
H	0.82094669	1.82895731	1.84820379
H	0.17845534	3.46758443	1.69572782
H	-0.89114568	2.06407564	1.51680161
H	1.37639792	2.83988495	-0.37469269
H	-2.82258178	-1.29389925	-1.34960083
H	-4.88091099	-1.14742145	-0.22168358
H	-4.04297042	-1.21344068	1.33200088
H	-4.00065027	0.27345517	0.37666456

H	-0.91075672	2.94718891	-1.79090035
H	-1.89070275	2.84827940	-0.32438641
H	-0.80793353	4.22618830	-0.56767108
C	0.21467488	2.65086306	1.47918173
H	0.99493027	2.07401589	1.96921476
H	0.39074564	3.70796935	1.67879598
H	-0.74274560	2.36764064	1.91364677
H	1.14125205	2.71052778	-0.46629134
H	-3.21458757	-2.33649915	-0.41443809
H	-4.49545506	-0.36822578	-0.53548258
H	-3.24773288	0.48994193	0.36944750
H	-2.92944274	-0.00715690	-1.29447944