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Photochemical Dynamics of E-iPr-Furylfulgide – Electronic Supplementary Information

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1 Benchmark Calculations

In this section, we report a detailed comparison between OM3/MR-CI and *ab-initio* results. We start with the energies of geometries encountered during trajectory runs. Thereafter we address the optimized geometries and the relative energies of the relevant minimum-energy conical intersections and local minima. While the *ab-initio* results serve as reference data for assessing the quality of the OM3/MR-CI results, we note that they should not be considered converged, neither with respect to the one-electron basis nor with respect to the many-electron basis (i.e., the active space). Because of the size of the present target molecule, further extension of the one-electron basis and/or the active space would render the *ab-initio* calculations intractable for all practical purposes. Taking these caveats into account, we generally find reasonable agreement between the OM3/MR-CI and *ab-initio* results in these benchmark calculations. We also note that there is good agreement between the OM3/MR-CI results and experiment for many observables (see main article). Taken together, this gives us confidence into the reliability of the adopted semi-empirical approach.

1.1 Transient Geometries

Snapshots were taken from two arbitrarily chosen trajectories for each of the three reaction paths mentioned in section **4.3** of the main article, a reactive and an unreactive one. Geometries from each of the six trajectories were extracted every 25 fs during the first picosecond, resulting in a total of 240 geometries. While these are likely not sufficiently representative for the full reaction swath, a significant fraction of them can still be expected to reside in regions of molecular configuration space that are relevant to the dynamics under study. The *ab-initio* reference data were obtained from CASPT2(14,13) calculations with a mixed basis as specified in the main article and an active space consisting of 14 electrons in 13 π-orbitals. The wavefunction was optimized for the best description of the four lowest singlet states (state-averaged over these four states) and the perturbative treatment was carried out in these four states (multi-state CASPT2) with a level shift of 0.2 Hartree. 120 of the 240 geometries were, regardless of the large active space and the applied level shift, contaminated by intruder states, leaving 120 transient geometries for the statistical evaluation. A complete list of the 120 geometries used in the benchmark calculations can be obtained from the corresponding author on enquiry. A statistical comparison between the OM3/MR-CI energies and the MS-CASPT2 reference energies is given in Table 1.

In the statistical evaluation, the ground-state energy was set to zero for the most stable geometry (which was the same for MS-CASPT2 and OM3/MR-CI). The resulting relative

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Table 1: Statistical comparison between OM3/MR-CI and MS-CASPT2 energies at transient geometries encountered during the dynamics (see text). MSD is the mean squared deviation. All energies are given in Hartrees.

type of data	max. deviation	av. deviation	MSD	standard deviation
ground state	0.0508	0.0129	0.000287	0.0169
1st excited state	0.0720	0.0178	0.000553	0.0235
2nd excited state	0.0518	0.0191	0.000502	0.0224
3rd excited state	0.0944	0.0336	0.001531	0.0391
all states	0.0944	0.0209	0.000718	0.0268
excitation energies	0.0693	0.0201	0.000627	0.0250

energies were then compared for all geometries and states to determine the difference between MS-CASPT2 and OM3/MR-CI for each point. Table 1 lists the largest deviation (max. deviation), the average absolute deviation (av. deviation), the mean squared deviation (MSD), and the standard deviation for each individual state, for all states together, and for all vertical excitation energies from the ground state. Inspection of the statistical data shows that the differences get larger with the level of excitation. For the dynamics studied presently, only the two lowest states are relevant, while the higher excited states contribute to the computed spectra. The average absolute deviations for the two lowest states are less than 0.5 eV and are thus reasonably small.

1.2 Stationary Points

Realistic molecular dynamics simulations require a realistic description of the relevant stationary points, even though quantitative accuracy in the corresponding structures and energies is only of secondary importance. In the following, we therefore compare *ab-initio* and semi-empirical results for key points on the energy landscapes encountered during the ring closure reaction.

At the semi-empirical level, the geometries were optimized using the standard OM3/MR-CI approach (see main article), except for the cyclic minimum structure, where convergence of the geometry optimization could be achieved only with a larger than the standard active space (i.e., using a (28,20) instead of a (18,17) active space, with the same reference configurations as usual). We note that the failure to find the cyclic ground-state minimum with the standard (18,17) active space is merely a technical problem: the minimum exists at the OM3/MR-CI level as a rather deep basin, since in the dynamics runs many trajectories end up in this basin and are trapped there for propagation times well into the picosecond regime (despite considerable excess energies corresponding to several hundred degrees Kelvin).

At the *ab-initio* level, the ground-state minima of both reactant and product were optimized

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at the MP2 level using Dunning's cc-pVTZ basis for carbon and oxygen, and cc-pVDZ for hydrogen. Excited-state geometries were obtained from CASSCF/6-31G(d) optimizations.

The comparisons between the *ab-initio* and semi-empirical results cover the three relevant ground-state minima and the three minimum-energy conical intersections (CI) that are relevant for the dynamics. They are restricted to the nine internal coordinates (six distances and three dihedral angles) depicted in Fig. 1, which are important for the reaction paths and change strongly during the reaction.

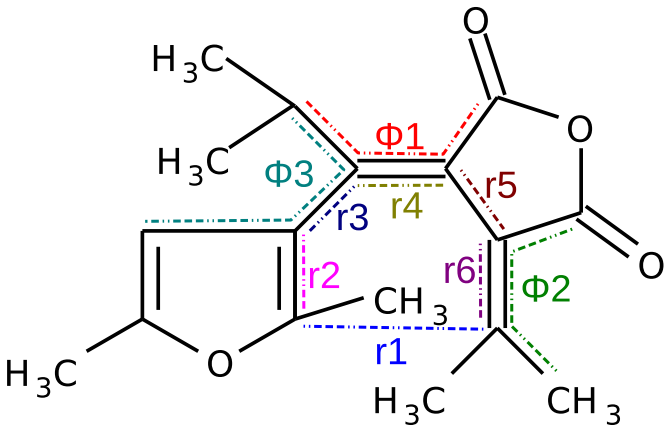

Figure 1: Schematic depiction of internal degrees of freedom used in the structural comparison of conical intersection and minimum-energy structures from *ab-initio* and OM3/MR-CI calculations.

The data in Tables 2 and 3 document the good qualitative agreement between the *ab-initio* and OM3/MR-CI results. In the case of the conical intersection structures, it is impossible to decide whether the rather small deviations arise from limitations of the OM3/MR-CI approach or from the CASSCF calculations (i.e., the use of a rather small active space and basis set as well as the lack of dynamic correlation). The results for the ground-state minima match very well and confirm the accuracy of the semi-empirical approach regarding geometrical aspects.

In addition to the geometries, the relative energies of the relevant stationary points were compared at the *ab-initio* and the semi-empirical level. The results are collected in Tables 4 and 5. The CASPT2 energies given in Table 5 are single-point energies at CASSCF

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Table 2: First part of the comparison of different conical intersections and stationary points at *ab-initio* and OM3/MR-CI levels. The coordinates are shown in Fig. 1.

structure	method	r1/Å	r2/Å	r3/Å	r4/Å	r5/Å
central ethylenic CI	OM3/MR-CI	4.45	1.42	1.44	1.43	1.43
	CASSCF(10,9)/6-31G(d)	4.28	1.43	1.38	1.46	1.46
zwitter ionic CI	OM3/MR-CI	2.04	1.47	1.44	1.40	1.42
	CASSCF(10,9)/6-31G(d)	1.94	1.44	1.49	1.35	1.44
terminal ethylenic CI	OM3/MR-CI	3.48	1.40	1.47	1.37	1.43
	CASSCF(10,9)/6-31G(d)	3.56	1.37	1.49	1.35	1.46
open ring minimum	OM3/MR-CI	3.44	1.40	1.46	1.37	1.47
	MP2/mixed basis	3.34	1.38	1.46	1.37	1.46
cyclic minimum	OM3/MR-CI	1.55	1.54	1.38	1.45	1.38
	MP2/mixed basis	1.53	1.52	1.37	1.44	1.37
unreactive minimum	OM3/MR-CI	4.16	1.40	1.47	1.37	1.47
	MP2/mixed basis	4.02	1.38	1.46	1.37	1.46

Table 3: Second part of the comparison of different conical intersections and stationary points at *ab-initio* and OM3/MR-CI levels. The coordinates are shown in Fig. 1.

structure	method	r6/Å	$\phi 1/^\circ$	$\phi 2/^\circ$	$\phi 3/^\circ$
central ethylenic CI	OM3/MR-CI	1.38	80	−2	22
	CASSCF(10,9)/6-31G(d)	1.36	90	2	3
zwitter ionic CI	OM3/MR-CI	1.44	16	19	31
	CASSCF(10,9)/6-31G(d)	1.45	5	19	52
terminal ethylenic CI	OM3/MR-CI	1.42	2	85	85
	CASSCF(10,9)/6-31G(d)	1.44	−1	96	75
open ring minimum	OM3/MR-CI	1.37	10	8	56
	MP2/mixed basis	1.36	14	12	49
cyclic minimum	OM3/MR-CI	1.53	5	39	12
	MP2/mixed basis	1.50	12	37	6
unreactive minimum	OM3/MR-CI	1.37	9	10	−114
	MP2/mixed basis	1.36	14	14	−122

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optimized structures (CASSCF//CASPT2) with no level shift applied in the two lowest electronic states (multi-state CASPT2). Table 4 indicates that OM3/MR-CI underestimates the stability of the cyclic product relative to the reactant and the unreactive isomer, consistent with the assumption in section **4.2** of the main paper that the reduced quantum yield compared to experiment may be a ground-state effect. Table 5 shows reasonable agreement between the *ab-initio* and semi-empirical results for the excited-state energetics.

Table 4: Energies (in kJ/mol) of optimized ground-state structures from OM3/MR-CI and MP2/cc-pVTZ(heavy atoms), cc-pVDZ(hydrogen).

method	reactant	cyclic product	unreactive isomer
OM3/MR-CI	7	0	15
MP2	55	0	67

Table 5: Energies (in kJ/mol) of optimized conical intersection structures from OM3/MR-CI, CASSCF(10,9)/6-31G(d,p), and CASPT2(14,13)/app-TZ.

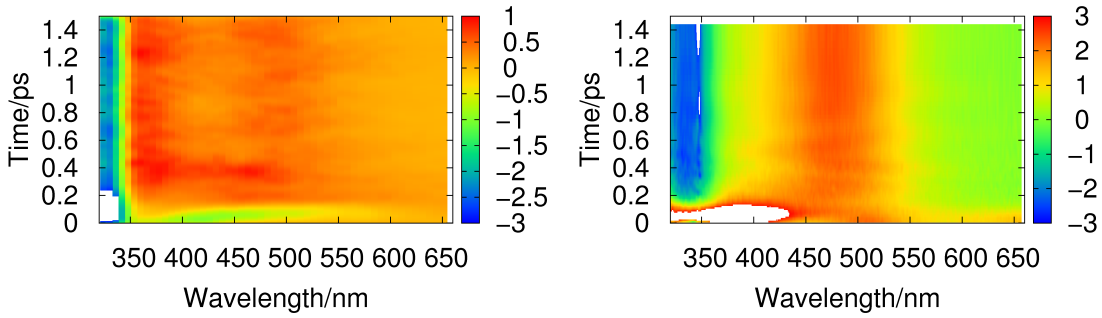
method	zwitterionic CI	central ethylenic CI	terminal ethylenic CI
OM3/MR-CI	6	0	40
CASSCF(10,9)	14	0	46
CASPT2(14,13)	-5	0	55

2 Comparison to experimental data

2.1 Simulation of transient spectra

The core of the validation against experiment in the present work is the comparison of simulated and experimental transient spectra. The simulation of the transient spectra is basically a straightforward process but deserves some explanation. An experimental transient absorption spectrum is measured as the difference UV/Vis spectrum of an excited volume of sample at a given time and an unexcited reference volume of the same sample. This gives the transient spectrum as the difference in optical density between excited transient and static UV/Vis spectrum (ΔOD). To simulate the transient spectrum in silico, we computed all relevant transition frequencies and squared transition dipole moments along the photo-excited trajectories at each time step of our simulation, covering all possible transitions from the currently populated state. The squared transition dipole moment was

taken to be positive in the case of absorption, and negative in the case of stimulated emission. This procedure effectively yielded a UV/Vis absorption spectrum for the whole swath of trajectories at each given time step. The resulting spectrum was divided by the number of trajectories for normalisation, and the transient spectrum at each time step was then obtained by subtracting the (also normalised) static spectrum of the reactant (calculated from the thermalisation runs without keeping the time information).



(a) simulated spectrum

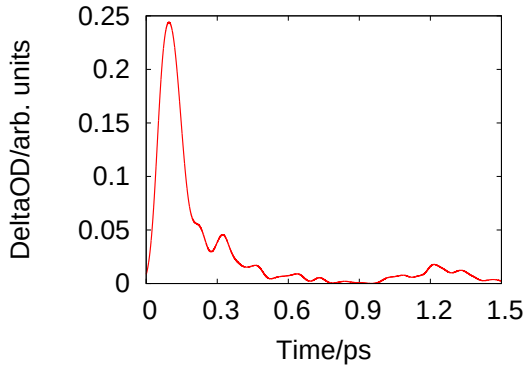
(b) experimental spectrum

Figure 2: Simulated (2a) and experimental [1] (2b) transient spectra of E-iPr-furylfulgide.

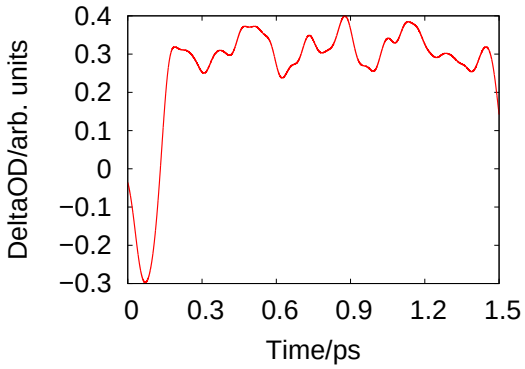
2.2 Comparison of spectral cuts

This section provides further details concerning the comparability of the simulated and experimental transient spectra. Fig. 2 depicts the simulated (2a) and experimental (2b) transient spectra already shown in the main body of the paper (reproduced here again for easy reference). Close inspection of these spectra reveals two important features. One is a small positive signal at the highest wavelengths at times below 150 fs. This component is the only excited-state absorption visible in the simulated spectrum, corresponding to an excitation from the first to the fifth excited state. A cut through this component for the experimental and the theoretical spectrum is depicted in Figs. 3c and 3a respectively. The signal in both spectra decays very fast and in approximately the same time.

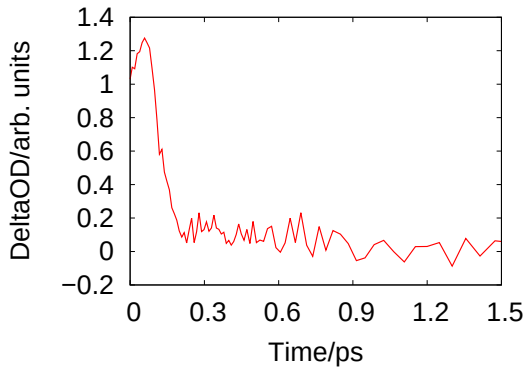
The other characteristic feature of the experimental spectrum is the oscillatory pattern in the newly formed product absorption at 480 nm. Although we cannot attribute this oscillation to a distinct degree of freedom of the molecule (e.g., a single normal mode or a combination of a few normal modes or a single local mode), a general rocking of the rather rigid cyclic molecule is clearly visible in our simulations. A cut through the right-hand side of the band in both spectra, see Figs. 3b(simulated) and 3d(experimental), shows good agreement. As already explained in the main body of the article (see section **4.2**), the different signs of the signal at short times can be attributed to the lack of highly



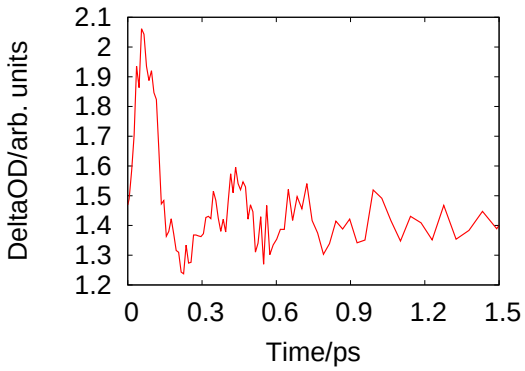
(a) simulated cut at 702 nm



(b) simulated cut at 522 nm



(c) experimental cut at 635 nm



(d) experimental cut at 525 nm

Figure 3: Simulated (3a and 3b) and experimental [1] (3c and 3d) cuts through transient spectra of E-iPr-furylfulgide.

excited states in the simulation. Since both the excited-state absorption and the stimulated emission are processes originating from the first excited state, they can be expected to lose intensity on a similar time scale, which is what they do. Afterwards, the oscillation in the product absorption band sets in on very similar time scales in the simulation and in the experiment, showing a comparable structure in both.

3 Coordinate files

The following sections list the coordinates of the structures from section 1.2 in xyz-format. All coordinates are given in Ångstrom.

3.1 Conical intersections

This section presents the optimized geometries of the minimum-energy conical intersections on both levels of theory currently applied.

```
41
central ethylenic CI CASSCF(10,9)/6-31g(d)
 C        -1.5790059190        0.6700673881        1.2338130803
 C        -0.2626186493        0.4793066595        0.8726798741
 C         0.4508710837       -0.2068273732        1.9502014587
 C        -0.6128596598       -0.3186000758        3.0128698380
 O        -1.7531830025        0.1860323623        2.5326162036
 C         0.1988909512        0.8671853765       -0.4623431998
 C         1.7161896433       -0.6793626954        2.0861350246
 C         2.7619653612       -0.5116463252        1.0071112010
 O        -0.5476629332       -0.7620517297        4.1110934247
 O        -2.5501117125        1.0837089884        0.6362027395
 C         0.0839720645       -0.0002903191       -1.5304396987
 C         0.4502455128        0.1305633263       -2.9428523099
 C         0.0182420656       -0.9677717529       -3.5745853815
 O        -0.6126644191       -1.7914883119       -2.6363988893
 C        -0.5906984731       -1.2635461962       -1.4704915882
 C         0.0449949961       -1.4880728765       -4.9670925185
 H         0.9686718599        0.9346930819       -3.4081500852
 H         3.7173554441       -0.2418803199        1.4492535915
 H         2.9244507328       -1.4397783839        0.4596205571
 H         2.5188842053        0.2569744140        0.2855500956
 H         0.5709737167       -2.4349607945       -5.0159407915
 H        -0.9613799894       -1.6373621210       -5.3416962954
 H         0.5506968224       -0.7776412041       -5.6073710010
 C         2.2420239851       -1.4150129956        3.2985847150
 H         2.7357290190       -2.3341431075        2.9855771179
 H         2.9971136112       -0.8146429701        3.8036196267
 H         1.4754096568       -1.6596815810        4.0124069525
 C        -1.2733942248       -2.0442880236       -0.4050093357
 H        -1.6164380237       -2.9776614427       -0.8305048423
 H        -0.6006274907       -2.2289136700        0.4188840440
 H        -2.1146066831       -1.4709183754       -0.0380830034
 C         0.7246706605        2.2934424892       -0.6033904329
 C         1.8432102336        2.5864976325       -1.6152602994
 C        -0.4812010356        3.2296820583       -0.8381732359
 H         1.1143488966        2.5172722960        0.3800928779
 H         2.5980794074        1.8074975343       -1.6483207064
 H         1.4691774458        2.7525939631       -2.6184753688
 H         2.3388388827        3.5030694270       -1.3146891448
 H        -0.1415184375        4.2583392780       -0.7754198481
 H        -0.9012745995        3.0725670143       -1.8269853809
 H        -1.2642177628        3.0706959995       -0.1123939434
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zwitter ionic CI CASSCF(10,9)/6-31g(d)
 C          0.2071123291      -0.7068385493      -2.6857723268
 C          0.2424254220      -0.4272557497      -1.2119813240
 C          0.2680374048       1.0135341895      -1.1230393480
 C          0.0152580647       1.5434191374      -2.3888531383
 O          0.0243742612       0.4530744098      -3.3047827142
 C          0.0397604119      -1.3060552432      -0.2023272732
 C          0.3765757004       1.7257305427       0.1323584434
 C          1.7451034440       1.7146687204       0.8072602271
 O         -0.1604302845       2.6411287481      -2.8339022706
 O          0.3044531140      -1.7446954034      -3.2523287627
 C         -0.0491417873      -0.6254581313       1.1225087407
 C          0.5737628551      -0.8895350751       2.3211334709
 C          0.2050535727       0.1499326724       3.1897668876
 O         -0.5699020560       0.9864271530       2.6131966100
 C         -0.7530111090       0.6252171510       1.2674210939
 C          0.6286748433       0.4118460596       4.5929723823
 H          1.2431266883      -1.6860751307       2.5641044311
 H          2.2473903245       0.7623394859       0.7181867899
 H          1.7194352905       2.0233261445       1.8483009788
 H          2.3448993915       2.4441743330       0.2735398221
 H          0.6318694046      -0.5117529158       5.1577170522
 H         -0.0329149221       1.1270573615       5.0609151714
 H          1.6377394903       0.8110483079       4.5959504490
 C         -0.2320698743       3.1179411824       0.1836739988
 H         -1.2358674531       3.1434882466      -0.2105692968
 H          0.3655841849       3.7579023558      -0.4538896512
 H         -0.2194653057       3.5200507574       1.1912541004
 C         -2.1869152925       0.8199488709       0.8377920893
 H         -2.8194410810       0.0378621859       1.2436282053
 H         -2.2437192026       0.7972236053      -0.2400563149
 H         -2.5519075032       1.7740223685       1.1923580450
 C         -0.1634650892      -2.8085902135      -0.3310890388
 C          1.0676495120      -3.6185924527       0.1015692221
 C         -1.4229294709      -3.2858382317       0.4053800899
 H         -0.3071841536      -2.9982043101      -1.3839809239
 H          1.9524804839      -3.2874237601      -0.4301637467
 H          0.9203327755      -4.6720823883      -0.1172066074
 H          1.2608631505      -3.5382771420       1.1686098335
 H         -1.3474201498      -3.1443128050       1.4812119660
 H         -1.5837716064      -4.3449940619       0.2314798836
 H         -2.3043837069      -2.7563000139       0.0569704584
```

41
terminal ethylenic CI CASSCF(10,9)/6−31g(d)

C	0.0074256148	−1.0391356105	−2.5911000090
C	−0.0307844052	−0.5021461835	−1.1815054919
C	−0.1762664608	0.9311346305	−1.4246285731
C	0.0639987489	1.2046018193	−2.7535916211
O	0.0778387483	−0.0023086438	−3.4414208982
C	0.0826121640	−1.1933161127	−0.0260499971
C	0.0823104247	2.0232559881	−0.5280310410
C	1.4572613596	2.4795720277	−0.2865493123
O	0.2410816192	2.2518864843	−3.3403069683
O	−0.0195375378	−2.1585789890	−2.9730340655
C	0.0202991840	−0.4114408626	1.2447908512
C	1.1133802646	−0.0761297569	2.1472847680
C	0.5736875218	0.6128936672	3.1794127617
O	−0.7627529792	0.7367451402	2.9955079064
C	−1.0914420874	0.1146947321	1.8368694000
C	1.1409248846	1.2292219056	4.4129872382
H	2.1462972821	−0.3297800033	2.0261289675
H	1.6665087766	2.9134263883	−1.2722552077
H	2.1252909401	1.6392952703	−0.1831265844
H	1.5794160958	3.2235036592	0.4864426815
H	2.2114786216	1.0701294046	4.4503305722
H	0.6982538827	0.7911521236	5.3012776861
H	0.9502472579	2.2975342279	4.4418347468
C	−0.9985046298	2.8889329310	−0.0984298138
H	−1.9477047071	2.3868554121	−0.0439654456
H	−1.0155403711	3.4511646447	−1.0533729393
H	−0.7861386807	3.5712154068	0.7108225286
C	−2.5474774040	0.0326298431	1.5216320570
H	−2.6917404953	−0.2930035536	0.5004071704
H	−3.0290274553	0.9955426587	1.6586613793
H	−3.0423474532	−0.6734034613	2.1807493253
C	0.2471105818	−2.7086945840	0.0577899737
C	1.5488161218	−3.1212195406	0.7595573896
C	−0.9601751622	−3.3682903936	0.7380149462
H	0.2923732605	−3.0817567632	−0.9526015399
H	2.4124584169	−2.6577168659	0.2911863357
H	1.6799526238	−4.1974703310	0.6983733986
H	1.5471212766	−2.8535440675	1.8118018367
H	−1.8793380537	−3.1349064331	0.2101117126
H	−1.0682190076	−3.0430611755	1.7692297838
H	−0.8476369776	−4.4485751906	0.7446502521

```
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central ethylenic CI OM3-GUGA-CI
 C        -0.0783529374        0.1170826574        1.6031865563
 C        -0.3542605846        0.8154391965        0.3252319271
 C        -1.7436895297        1.1682829399        0.3084148622
 C        -2.3062030397        0.6598305189        1.6059124726
 O        -1.2769044764        0.0544776705        2.3546645168
 C         0.6555337457        0.8846616515       -0.6873035076
 C        -2.5122041785        1.8667918515       -0.6026609775
 C        -1.9014324358        2.4042486398       -1.8624515068
 O        -3.4346801456        0.7063408260        2.0827217305
 O         0.9634274594       -0.3444139419        2.0641865665
 C         1.5643071679        1.9960059115       -0.6597691477
 C         2.5311987451        2.4092754426       -1.6815662652
 C         3.1706832086        3.5370162211       -1.1996190638
 O         2.6591411239        3.8882126936        0.0511552456
 C         1.6914631014        2.9615845241        0.3773161744
 C         4.2177499441        4.4359334429       -1.7472359083
 H         2.7129784822        1.9128594359       -2.6254299792
 H        -1.6854379195        1.5677908175       -2.5546972737
 H        -2.5938442477        3.1023568236       -2.3599091598
 H        -0.9507085656        2.9201904414       -1.6562913138
 H         3.8239734734        4.9754663948       -2.6232937706
 H         4.5167459199        5.1728634700       -0.9827834979
 H         5.0944470404        3.8374549837       -2.0436250886
 C        -3.9587381413        2.1090451649       -0.3625398160
 H        -4.1044948699        2.7446943848        0.5293337720
 H        -4.4378537309        2.6123557260       -1.2223479126
 H        -4.4961030731        1.1631514896       -0.1761941407
 C         1.0653577596        3.1338247052        1.7054316361
 H         1.3929315878        4.0809388318        2.1578518331
 H        -0.0314612406        3.1455527474        1.6077638930
 H         1.3640711757        2.3038299552        2.3625159059
 C         0.8438360125       -0.3413168101       -1.5607066415
 C         0.7146889411       -0.0370024774       -3.0555009599
 C         2.1850777471       -0.9876680606       -1.2155015065
 H         0.0144089009       -1.0724755415       -1.2964102837
 H        -0.2484538550        0.4589708609       -3.2774932995
 H         1.5351132094        0.6129180365       -3.4089224509
 H         0.7587861028       -0.9811093365       -3.6288479806
 H         2.3076866051       -1.9241717586       -1.7834418191
 H         3.0254202740       -0.3206273220       -1.4683468670
 H         2.2433750791       -1.2201785417       -0.1422009991
```

```
41
zwitter ionic CI OM3-GUGA-CI
 C        -1.5180101478      -0.8153658883      -0.2787897334
 C        -0.6074763206       0.3656341549      -0.4079436811
 C        -1.3451809798       1.5119680401       0.0735603917
 C        -2.5812066387       1.0075510294       0.6795098974
 O        -2.6779788661      -0.3953920254       0.3749231810
 C         0.7538558510       0.3669378266      -0.6574222680
 C        -0.8806655435       2.8721037649       0.0482279583
 C        -0.6633041919       3.4454926390      -1.3458648170
 O        -3.5220156674       1.5418343479       1.2633292000
 O        -1.3946568493      -1.9821053409      -0.6328212472
 C         1.3983583310       1.6452252142      -0.3652387936
 C         2.3504154401       2.3648024256      -1.1344309116
 C         2.4573689834       3.6483914199      -0.5705199563
 O         1.6292164732       3.7859177016       0.5185970208
 C         0.8588549786       2.5816972600       0.6536939293
 C         3.2278768624       4.8508645483      -0.9777592055
 H         2.9074762027       1.9981574195      -1.9815356010
 H        -0.1887147074       2.7312658598      -2.0337094139
 H        -0.0615091327       4.3672283883      -1.3190861878
 H        -1.6577420697       3.7010477221      -1.7523291086
 H         4.1186613896       4.5412762849      -1.5511102329
 H         3.5525432609       5.4214874755      -0.0966036444
 H         2.5880222537       5.4891895410      -1.6083742026
 C        -1.5583079847       3.8459387005       0.9836150799
 H        -1.7159593392       3.4158304747       1.9845391411
 H        -2.5546175236       4.1075596333       0.5847930150
 H        -0.9661767278       4.7675904703       1.0901542937
 C         0.8135780199       2.1926055719       2.1063363100
 H         1.8265082864       1.8947035586       2.4368198140
 H         0.1279074084       1.3478143102       2.2625651068
 H         0.4899147642       3.0419161129       2.7283315691
 C         1.5256554980      -0.8353652289      -1.1509986573
 C         1.6700098798      -0.7702282675      -2.6666560830
 C         2.8772863958      -0.9336344350      -0.4338156220
 H         0.9191614008      -1.7550209118      -0.8871072798
 H         0.6912706217      -0.6930789382      -3.1677996667
 H         2.1704225688      -1.6814067124      -3.0425712125
 H         2.2849736122       0.0967389708      -2.9791406567
 H         3.5429220269      -0.0981824232      -0.7138298438
 H         3.3819988255      -1.8698603753      -0.7307686559
 H         2.7594675861      -0.9394330979       0.6597691947
```

```
41
terminal ethylenic CI OM3-GUGA-CI (unconverged)
 C          0.0000000000        0.0000000000        0.0000000000
 C          1.5111523824        0.0000000000        0.0000000000
 C          1.8781912515        1.3837030443        0.0000000000
 C          0.6581229355        2.1953735919       -0.0086743731
 O         -0.4386143999        1.3124011679        0.0214156164
 C          2.2831163810       -1.1305698445       -0.0445922071
 C          3.1703298886        1.9797691725       -0.0134175746
 C          3.8310148434        2.3573198837       -1.2955799318
 O          0.4669001449        3.4089951394       -0.0035741406
 O         -0.7918254729       -0.9364337956       -0.0093846757
 C          3.7460738614       -0.9945366841       -0.1093320554
 C          4.5410944234       -0.9094118483       -1.3198684303
 C          5.8637933504       -0.8745122361       -0.9127795411
 O          5.9370316985       -0.9188844061        0.4792808495
 C          4.6622263905       -1.0181655692        0.9480386206
 C          7.1527749568       -0.7655759819       -1.6401796335
 H          4.1482411757       -0.8570598200       -2.3317631937
 H          3.2571703437        1.9870335432       -2.1596096720
 H          4.8413503366        1.9222751413       -1.3379662621
 H          3.9093026025        3.4535704148       -1.3593988686
 H          6.9894066482       -0.9335438142       -2.7154219239
 H          7.8630415879       -1.5183660205       -1.2595116492
 H          7.5879784491        0.2416045773       -1.4833487426
 C          3.8003680259        2.4061128773        1.2691531929
 H          3.6058044234        1.6650485638        2.0523901718
 H          3.3263423194        3.3549403772        1.5742338368
 H          4.8855765780        2.5528147120        1.1607460973
 C          4.5475153348       -1.1667224234        2.4190821454
 H          3.4931734839       -1.0657441248        2.7229198353
 H          5.1541495351       -0.3942019160        2.9275338312
 H          4.9234374676       -2.1632176025        2.7224437002
 C          1.6995092219       -2.5352260096       -0.1336416655
 C          1.7355713257       -2.9983170772       -1.5900779422
 C          2.4466459405       -3.5152493846        0.7809803179
 H          0.6257340168       -2.4965355622        0.2208605735
 H          1.2142519647       -2.3050747280       -2.2662306398
 H          1.2379988258       -3.9780276393       -1.6820429698
 H          2.7744656670       -3.0952062031       -1.9483543193
 H          2.4074021088       -3.2079815664        1.8377153796
 H          3.5044961056       -3.5926693031        0.4716208362
 H          1.9897978758       -4.5204601769        0.7064380608
```

3.2 Stationary points

This section presents the optimized stationary points discussed in section 1.2.

```
   41
mp2 optimised E-iPr-Furylfulgide (reactive configuration)
 C     -1.132849     -0.855627      0.360903
 C     -0.518352      0.445197     -0.005138
 C     -1.539267      1.445335      0.305116
 C     -2.456067      0.780158      1.265279
 O     -2.219302     -0.591232      1.191060
 C      0.799576      0.590488     -0.334931
 C     -1.825985      2.619204     -0.311785
 C     -1.043245      3.104720     -1.486215
 O     -3.299606      1.207595      2.004207
 O     -0.842484     -1.988128      0.085190
 C      1.421844      1.908631     -0.314598
 C      2.276233      2.514832     -1.293963
 C      2.632775      3.738080     -0.807827
 O      2.074696      3.922338      0.425732
 C      1.341880      2.810458      0.724036
 C      3.469681      4.842494     -1.329788
 H      2.565476      2.114501     -2.254440
 H     -1.718618      3.603884     -2.190547
 H     -0.289851      3.842340     -1.175638
 H     -0.516707      2.295365     -1.997566
 H      3.853576      4.574504     -2.316798
 H      2.892585      5.768839     -1.420769
 H      4.319758      5.039661     -0.668001
 C     -2.963311      3.502742      0.093518
 H     -3.482344      3.157545      0.985200
 H     -2.577129      4.515651      0.270854
 H     -3.677045      3.586989     -0.736118
 C      0.679924      2.788891      2.045635
 H     -0.251572      3.369623      2.043051
 H      0.428165      1.760083      2.317946
 H      1.343907      3.205796      2.809402
 C      1.673283     -0.599507     -0.660863
 C      1.604545     -0.897176     -2.161931
 C      3.113010     -0.425231     -0.188881
 H      1.248296     -1.468338     -0.150606
 H      0.574128     -1.105693     -2.466353
 H      1.980093     -0.055511     -2.754344
 H      2.217357     -1.774188     -2.398248
 H      3.655108     -1.367692     -0.321461
 H      3.640204      0.351078     -0.750571
 H      3.152645     -0.156673      0.872252
```

41
OM3 optimised E–iPr–Furylfulgide (reactive configuration)

C	−1.1588809818	−0.8786762383	0.2389559113
C	−0.5336996265	0.4530712666	−0.0833616417
C	−1.5770258096	1.4407759123	0.2275856655
C	−2.5408266364	0.7239334867	1.1416285815
O	−2.2712781267	−0.6708941904	1.0659466473
C	0.8071863368	0.5985474102	−0.3418958747
C	−1.8530912014	2.6839280203	−0.2839939749
C	−1.0421262349	3.2977679786	−1.3751233338
O	−3.4392352401	1.1164017900	1.8734993009
O	−0.8037028543	−2.0153610338	−0.0441500146
C	1.4279959232	1.9242161830	−0.3231975726
C	2.2580854654	2.5182727275	−1.3547134376
C	2.6910217891	3.7415579215	−0.8699296262
O	2.2146071123	3.9408005038	0.4286647712
C	1.4315955711	2.8366516282	0.7424830091
C	3.5436248891	4.8218400917	−1.4209207847
H	2.4519238698	2.0840105667	−2.3252070619
H	−1.7061755251	3.8260199512	−2.0803197902
H	−0.3345707845	4.0338835014	−0.9476533822
H	−0.4714017267	2.5448734354	−1.9404542279
H	3.8551600148	4.5745849443	−2.4466778597
H	2.9830772211	5.7685924815	−1.4348541102
H	4.4347988114	4.9427007764	−0.7923083800
C	−3.0407657958	3.4678039174	0.1756424807
H	−3.2258067577	3.3326499731	1.2508657458
H	−2.9040607755	4.5424796683	−0.0261923775
H	−3.9392426281	3.1218457619	−0.3650980041
C	0.8192794068	2.8367812096	2.0904686957
H	−0.1422973789	3.3766292392	2.0604894306
H	0.6425127538	1.8056297620	2.4312397725
H	1.4854373435	3.3405598605	2.8063270526
C	1.7323755744	−0.6001414393	−0.5429904111
C	1.6161084817	−1.0721123906	−1.9919712536
C	3.1924750635	−0.2737942991	−0.1988213891
H	1.3826588971	−1.4176677449	0.1496301779
H	0.5838923557	−1.3751779791	−2.2445608098
H	1.9224971779	−0.2822512972	−2.7077768730
H	2.2622182236	−1.9579260742	−2.1564661184
H	3.7770273652	−1.2153573837	−0.2193434792
H	3.6532741903	0.4158904917	−0.9262531568
H	3.2734878386	0.1660422327	0.8074860625

```
41
mp2 optimised cyclic product
 C      -1.1213159957    -0.9001692055     0.8059926102
 C      -0.3709523663     0.3302018380     0.4269096605
 C      -1.2165390028     1.3847505298     0.6196521874
 C      -2.5241208062     0.8599311232     1.0161951036
 O      -2.4097091824    -0.5311320786     1.1564106685
 C       0.9515671366     0.4408952910    -0.1260338298
 C      -0.8628379801     2.7970167089     0.2660840249
 C      -1.1999534178     2.9929135417    -1.2215007048
 O      -3.5728523758     1.4178633379     1.1994754738
 O      -0.7654702192    -2.0470340363     0.8483999813
 C       1.3885074252     1.7367220553    -0.2261315143
 C       2.4854221713     2.3717649016    -0.8833714552
 C       2.2959044461     3.7181934631    -0.7923504532
 O       1.1915479125     4.0775915481    -0.0985190935
 C       0.6507307087     2.8579524913     0.4834923349
 C       3.0887751624     4.8377187704    -1.3462688066
 H       3.2969056212     1.9141732083    -1.4291142352
 H      -0.9517046674     4.0110863279    -1.5360698371
 H      -0.6427384885     2.2849889232    -1.8456647666
 H      -2.2717145087     2.8306802642    -1.3736951909
 H       3.9400538829     4.4609613146    -1.9161576481
 H       2.4618006639     5.4549911274    -1.9988241294
 H       3.4519642245     5.4792946296    -0.5359345772
 C      -1.6038040159     3.8352211739     1.1038271596
 H      -2.6644294944     3.8378443304     0.8421165143
 H      -1.5300192427     3.6256976248     2.1743282622
 H      -1.1858488911     4.8285451147     0.9056627576
 C       1.0717944732     2.8558623600     1.9497055391
 H       0.6890700106     1.9633163245     2.4548164042
 H       2.1653748527     2.8434991021     1.9991593701
 H       0.7040130757     3.7503123313     2.4587125108
 C       1.7008557935    -0.7558171710    -0.6595955472
 C       1.7522282731    -0.7281215410    -2.1878117020
 C       3.0958570837    -0.8654549490    -0.0485078392
 H       1.1412078277    -1.6461431371    -0.3609569864
 H       0.7433855959    -0.6904978330    -2.6123916976
 H       2.3035733823     0.1444578783    -2.5534638333
 H       2.2487679709    -1.6271376719    -2.5696288952
 H       3.5969545830    -1.7713403065    -0.4067737400
 H       3.7222631071    -0.0076273525    -0.3131018412
 H       3.0385792703    -0.9159693530     1.0436227609
```

```
   41
OM3 representative geometry of cyclic product
 C      0.000000      0.000000      0.000000
 C      1.542483      0.000000      0.000000
 C      2.281832      1.164802      0.000000
 C      1.476068      2.345005      0.250570
 C      0.184720      2.305814      0.741211
 C     -0.603683      1.019883      0.994919
 O     -0.389123     -1.351084      0.343278
 C      0.771852     -2.127375      0.282189
 C      1.915953     -1.392110      0.055400
 C     -0.234651      3.713263      1.103904
 O      0.812197      4.597577      0.719824
 C      1.905635      3.802802      0.262829
 C      3.787101      1.288586     -0.181260
 C      4.245212      0.589500     -1.458116
 C     -0.324203      0.586442      2.442112
 C     -2.089928      1.231120      0.761903
 O      2.952523      4.350838     -0.074586
 O     -1.248925      4.148374      1.642097
 C      0.565044     -3.572781      0.540734
 C     -0.470604      0.191528     -1.460830
 C      4.467671      0.749672      1.074603
 H      4.045728      2.382392     -0.302963
 H      4.259919     -0.321155      1.232074
 H      5.553635      0.869372      0.966053
 H      4.121923      1.278565      1.975532
 H      4.073709     -0.499299     -1.384601
 H      3.720631      0.964749     -2.362294
 H      5.322732      0.769094     -1.658500
 H     -1.537761     -0.029408     -1.508355
 H     -0.277600      1.223021     -1.789066
 H      0.094076     -0.468913     -2.125793
 H      0.762962      0.453087      2.621484
 H     -2.278518      1.652408     -0.246242
 H     -0.704877      1.348038      3.140334
 H     -0.837996     -0.373249      2.636599
 H     -2.630703      0.274001      0.842670
 H     -2.501551      1.914211      1.517209
 H      1.525235     -4.111092      0.528805
 H      0.084840     -3.720727      1.515215
 H     -0.095501     -3.983817     -0.239418
 H      2.922485     -1.776939     -0.024281
```

41
mp2 optimised E–iPr–Furylfulgide (unreactive configuration)

C	−2.2829095481	1.8218522878	−0.8154750081
C	−0.8933941553	1.3331163773	−0.6501285508
C	−0.9028017972	−0.0389915592	−1.1440543925
C	−2.1336725516	−0.1543059136	−1.9670051150
O	−2.9450327531	0.9386772472	−1.6631319270
C	0.1641301130	2.1494765778	−0.3564645987
C	−0.1556550207	−1.1037531076	−0.7543922789
C	0.8432045296	−1.0050473030	0.3501189558
O	−2.5070204985	−0.9812386611	−2.7521419779
O	−2.8448277615	2.7966221877	−0.3933420031
C	1.5110376784	1.6903456059	−0.6961607596
C	1.8821896829	1.1703195109	−1.9800284813
C	3.2096457895	0.8653496730	−1.9212788212
O	3.6861996017	1.1466588283	−0.6708971480
C	2.6558877052	1.6517433567	0.0674677742
C	4.1871086414	0.3457005470	−2.9047384942
H	1.2396970620	1.0640895019	−2.8428842391
H	0.8309197738	−1.9355534469	0.9293589005
H	1.8582636357	−0.8823366596	−0.0541527089
H	0.6411784632	−0.1607771834	1.0140934444
H	4.9799083207	1.0762043992	−3.0985473917
H	4.6587653800	−0.5752010102	−2.5458783306
H	3.6766368369	0.1305815025	−3.8463241144
C	−0.3022065482	−2.4677633618	−1.3494872748
H	0.6861536927	−2.8087482078	−1.6860372159
H	−0.6274852823	−3.1765020411	−0.5770431659
H	−0.9964050036	−2.5002171162	−2.1864727310
C	2.9595244082	1.9281704097	1.4890397633
H	3.4334755451	1.0558023892	1.9530930371
H	3.6421129330	2.7787344700	1.6019122770
H	2.0391403952	2.1480754113	2.0317262600
C	−0.0622583949	3.5694067514	0.1258177131
C	−0.4888453212	3.6019472227	1.5963699330
C	1.1231532369	4.4925589421	−0.1268599792
H	−0.9170976307	3.9539229157	−0.4440886558
H	−1.3663359898	2.9718953816	1.7621165678
H	0.3183095261	3.2658371327	2.2552582634
H	−0.7467912848	4.6271942831	1.8839906700
H	0.8333179712	5.5229237547	0.1053600526
H	1.9823500261	4.2391967549	0.5008157103
H	1.4474395933	4.4550461492	−1.1715289590

41
om3 optimised E–iPr–Furylfulgide (unreactive configuration)

C	−2.3604374315	1.5920654211	−0.8760046913
C	−0.8823668605	1.3466345898	−0.7001365892
C	−0.6864914431	−0.0660845111	−1.0499420836
C	−1.9454427401	−0.4878822236	−1.7591638687
O	−2.9215076899	0.5409450014	−1.5965032111
C	0.0170987738	2.3688576485	−0.5226644543
C	0.2679312525	−0.9818369229	−0.6851937419
C	1.3496916950	−0.6687936028	0.2936181900
O	−2.2585286609	−1.4862357061	−2.3937979805
O	−3.0424863226	2.5514389619	−0.5336021961
C	1.4443912595	2.1196005005	−0.7597204216
C	1.9483421614	1.6260993727	−2.0399032865
C	3.3330592181	1.6517012773	−1.9555387612
O	3.7327391376	2.0894192036	−0.6973600185
C	2.5775501809	2.4022560632	0.0110622597
C	4.4193890586	1.3100454247	−2.9047614376
H	1.3325133352	1.3247666614	−2.8773272971
H	1.5583954969	−1.5501133227	0.9243109671
H	2.2772406126	−0.4013616118	−0.2494902573
H	1.0713020837	0.1633068124	0.9605440494
H	5.0009571708	2.2105799721	−3.1334983573
H	5.0826702340	0.5583846699	−2.4577104864
H	3.9950833585	0.9034626446	−3.8349915516
C	0.2025057643	−2.3995091674	−1.1620446130
H	1.1827682536	−2.8923404348	−1.0648216316
H	−0.5363104633	−2.9599999515	−0.5589397440
H	−0.1130081491	−2.4559583775	−2.2130709753
C	2.8034931869	2.8121665407	1.4176269642
H	3.3415553676	2.0080760154	1.9509866573
H	3.4061857775	3.7350783798	1.4456827697
H	1.8418457567	2.9942012264	1.9286808515
C	−0.4286332392	3.8111256314	−0.2823533886
C	−0.8184338668	3.9789547624	1.1836604769
C	0.6455056167	4.8305119134	−0.6811496708
H	−1.3351403652	3.9879868120	−0.9296640781
H	−1.6621642515	3.3241106638	1.4644309482
H	0.0342093120	3.7475361853	1.8593531723
H	−1.1401010573	5.0212293354	1.3792592976
H	0.2001918590	5.8430988658	−0.6466062435
H	1.5050205153	4.8243751921	0.0099874446
H	1.0107458545	4.6516612189	−1.7043904722

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