Supporting Information

Carbo-[3]oxocarbon and its isomers: evaluation of the stability and of the electron delocalization

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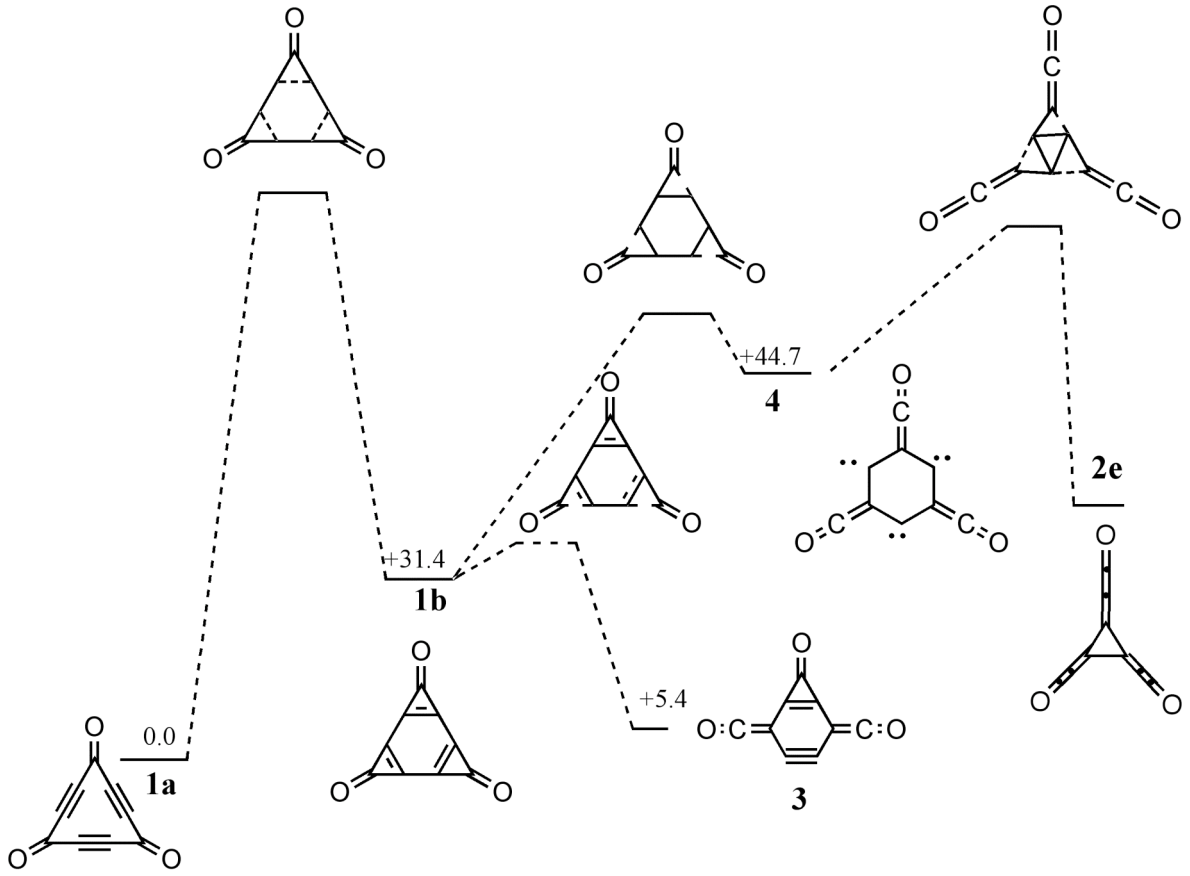

Figure S1. Possible interconversion pathways between isomers **1-4**. Relative Gibbs energies of C_9O_3 isomers in kcal/mol calculated at MP2/6-311+G* level.

Figure S1 displays possible interconversion pathways that have been envisioned in order to evaluate the possibility of isomerization of **1a** once it would have been synthesized. It was however not possible to obtain the true transitions states (i.e. first-order saddle points) of figure S1. For example, only second-order saddle points were isolated on the investigated reaction pathways describing the conversion of **1a** into **1b**. The description of these pathway may indeed be difficult even at the MP2 level of calculation, because it rather requires a multiconfigurational wavefunction. We therefore have to rely on thermodynamics only, that at least suggest that, once synthesized, the experimental target **1a** should be protected against subsequent isomerization.

1a B3PW91/6-311+G*, singlet spin state, D_{3h}, NImag=0

E = -568.246533; ZPE_CORR = -568.189997;
Gibbs free energy = -568.224251

C	1.966728	1.135491	0.000000
C	0.608120	1.673837	-0.000000
C	-0.608120	1.673837	-0.000000
C	-1.966728	1.135491	-0.000000
C	-1.753646	-0.310271	-0.000000
C	-1.145526	-1.363566	0.000000
C	-0.000000	-2.270982	-0.000000
C	1.145526	-1.363566	-0.000000
C	1.753646	-0.310271	-0.000000
O	3.005888	1.735450	0.000000
O	-0.000000	-3.470901	0.000000
O	-3.005888	1.735450	-0.000000

1a MP2/6-311+G*, singlet spin state, C_1, NImag=0
E = -567.010789; ZPE_CORR = -566.957694;
Gibbs free energy = -566.999056

C	1.978217	1.142314	0.033989
C	0.619032	1.687834	0.017170
C	-0.619087	1.687606	-0.021950
C	-1.978325	1.142274	-0.044205
C	-1.771263	-0.307707	-0.032426
C	-1.151578	-1.380287	-0.026317
C	0.000013	-2.284561	0.010462
C	1.152267	-1.380259	0.017349
C	1.771144	-0.307660	0.050339
O	3.029074	1.749177	0.035150
O	-0.000447	-3.497919	0.028955
O	-3.028941	1.749077	-0.067414

1a triplet spin state, C_{2v}, NImag=0
E = -568.159835; ZPE_CORR = -568.105880;
Gibbs free energy = -568.142192
$\langle S^2 \rangle$ = 2.024

C	0.000000	1.158947	1.377059
C	0.000000	1.775544	0.313873
C	0.000000	1.980666	-1.116959
O	0.000000	3.011288	-1.739044
C	0.000000	0.000000	2.149096
O	0.000000	0.000000	3.465854
C	0.000000	-1.158947	1.377059
C	0.000000	-1.775544	0.313873
C	0.000000	-1.980666	-1.116959
O	0.000000	-3.011288	-1.739044
C	0.000000	0.607901	-1.640365
C	0.000000	-0.607901	-1.640365

1b B3PW91/6-311+G*, singlet spin state, D_{3h}, NImag=0
E = -568.233912; ZPE_CORR = -568.176249;
Gibbs free energy = -568.209961

O	0.000000	3.680486	0.000000
C	0.000000	2.494980	0.000000
C	0.689398	1.217938	0.000000
C	1.399464	-0.011933	0.000000
C	2.160716	-1.247490	0.000000
O	3.187394	-1.840243	0.000000
C	0.710066	-1.206005	0.000000
C	-0.710066	-1.206005	0.000000
C	-2.160716	-1.247490	0.000000
O	-3.187394	-1.840243	0.000000
C	-1.399464	-0.011933	0.000000
C	-0.689398	1.217938	0.000000

1b MP2/6-311+G*, singlet spin state, D_{3h}, NImag=0
E = -566.970387; ZPE_CORR = -566.914802;
Gibbs free energy = -566.949098

O	2.622157	2.622157	0.000000
C	1.778960	1.778960	0.000000
C	0.369531	1.361933	0.000000
C	-1.000990	0.994703	0.000000
C	-2.430104	0.651144	0.000000
O	-3.581933	0.959776	0.000000
C	-1.364234	-0.360943	0.000000
C	-0.360943	-1.364234	0.000000
C	0.651145	-2.430104	0.000000
O	0.959776	-3.581933	0.000000
C	0.994703	-1.000990	0.000000
C	1.361933	0.369531	0.000000

1b UB3PW91/6-311+G*, triplet spin state, C_1, NImag=0
E = -568.215449; ZPE_CORR = -568.159465;
Gibbs free energy = -568.196378
$\langle S^2 \rangle$ = 2.025

C	-0.853592	0.594045	0.000257
C	0.373483	1.189255	0.002030
C	1.546491	0.400491	0.002008
C	1.346601	-1.005546	0.000116
C	0.139821	-1.615653	-0.001238
C	-1.074034	-0.839613	-0.000783
C	-0.779949	2.048205	0.000004
O	-1.307793	3.113437	-0.001291
C	2.699762	-0.400913	0.000194
O	3.877068	-0.579687	-0.000908
C	-2.316942	-1.358591	-0.001299
O	-3.380507	-1.792510	0.001233

2a B3PW91/6-311+G*, singlet spin state, D_{3h},
NImag = 3 (-78.3 cm^{-1}; -34.2 cm^{-1}; -34.1 cm^{-1})
E = -568.247176; ZPE_CORR = -568.193703;
Gibbs free energy = -568.228588

O	0.000000	4.592264	0.000000
C	0.000000	3.422863	0.000000
C	0.000000	2.149670	0.000000
C	0.000000	0.833298	0.000000
C	0.721657	-0.416649	0.000000
C	-0.721657	-0.416649	0.000000
C	-1.861669	-1.074835	0.000000
C	-2.964287	-1.711432	0.000000
O	-3.977018	-2.296132	0.000000
C	1.861669	-1.074835	0.000000
C	2.964287	-1.711432	0.000000
O	3.977018	-2.296132	0.000000

Single point **MP2/6-311+G*//B3PW91/6-311+G*** E = -566.963441

2b B3PW91/6-311+G*, singlet spin state, C_{2v},
NImag=1(-46.6 cm^{-1})
E = -568.248812; ZPE_CORR = -568.194985;
Gibbs free energy = -568.233552

O	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.169455
C	0.000000	0.000000	-2.442453
C	0.000000	0.000000	-3.757999
C	0.000000	0.715712	-5.015308
C	0.000000	-0.715712	-5.015308
C	0.000000	-1.856038	-5.695949
C	0.000000	-3.148974	-5.628160
O	0.000000	-4.304932	-5.758343
C	0.000000	1.856038	-5.695949
C	0.000000	3.148974	-5.628160
O	0.000000	4.304932	-5.758343

Single point **MP2/6-311+G*//B3PW91/6-311+G*** E = -566.969284

2c B3PW91/6-311+G*, singlet spin state, C_s,
NImag=1 (-49.3 cm^{-1})
E = -568.248759; ZPE_CORR = -568.194685;
Gibbs free energy = -568.233708

C	-1.320351	0.000000	-3.206964
C	-1.317289	0.000000	-1.912169
C	-0.575173	0.000000	-0.810825
C	0.702919	0.000000	-0.150174
C	2.026414	0.000000	-0.240252
C	3.151700	0.000000	0.400116
O	4.243002	0.000000	0.802606
O	-1.514083	0.000000	-4.353809
C	-0.518046	0.000000	0.626561
C	-1.116169	0.000000	1.799789
C	-1.698073	0.000000	2.931668
O	-2.230868	0.000000	3.972892

Single point **MP2/6-311+G*//B3PW91/6-311+G*** E = -566.950631

2d & 2d' B3PW91/6-311+G*, singlet spin state, C_s, NImag=0
E = -568.249469; ZPE_CORR = -568.195246;
Gibbs free energy = -568.235662

O	-3.566338	-2.595577	0.000000
C	-2.498626	-2.132385	0.000000
C	-1.245471	-1.813090	0.000000
C	-0.339556	-0.843635	0.000000
C	1.034317	-0.437422	0.000000
C	0.000000	0.564829	0.000000
C	-0.343828	1.844549	0.000000
C	-1.287503	2.727856	0.000000
O	-2.002221	3.646514	0.000000
C	2.319144	-0.778016	0.000000
C	3.539583	-0.344244	0.000000
O	4.685015	-0.142269	0.000000

Single point **MP2/6-311+G*//B3PW91/6-311+G*** E = -566.972028

2e B3PW91/6-311+G*, singlet spin state, C_{3h}, NImag=0
E = -568.249630553; ZPE_CORR = -568.195255;
Gibbs free energy = -568.234547

O	-1.096938	4.329399	0.000000
C	-0.649940	3.255566	0.000000
C	0.037550	2.158432	0.000000
C	0.000000	0.831534	0.000000
C	0.720130	-0.415767	0.000000
C	-0.720130	-0.415767	0.000000
C	-1.888032	-1.046697	0.000000
C	-2.494433	-2.190648	0.000000
O	-3.200901	-3.114676	0.000000
C	1.850482	-1.111735	0.000000
C	3.144373	-1.064918	0.000000
O	4.297839	-1.214723	0.000000

Single point **MP2/6-311+G*//B3PW91/6-311+G*** E = -566.972522

2T UB3PW91/6-311+G*, triplet spin state, C_s, NImag=0
E = -568.253824; ZPE_CORR = -568.200109;
Gibbs free energy = -568.241208
$\langle S^2 \rangle$ = 2.025

O	-3.452957	-2.953996	0.000000
C	-2.447118	-2.363255	0.000000
C	-1.315664	-1.772921	0.000000
C	-0.312997	-0.933319	0.000000
C	0.000000	0.563189	0.000000
C	0.980924	-0.437891	0.000000
C	2.307580	-0.729137	0.000000
C	3.480349	-0.199048	0.000000
O	4.605281	0.116585	0.000000
C	-0.534119	1.752536	0.000000
C	-1.237556	2.817789	0.000000
O	-1.843373	3.813953	0.000000

Single point **ROMP2/6-311+G*//B3PW91/6-311+G*** E = -566.967849

3 B3PW91/6-311+G*, singlet spin state, C_{2v}, NImag=0
E = -568.262493; ZPE_CORR = -568.205352;
Gibbs free energy = -568.240967

C	0.000000	1.536262	-0.583856
C	0.000000	0.675197	0.611682
C	0.000000	0.612898	-1.683572
C	0.000000	-0.612898	-1.683572
C	0.000000	-1.536262	-0.583856
C	0.000000	-0.675197	0.611682
C	0.000000	0.000000	1.894319
C	0.000000	-2.865950	-0.582147
O	0.000000	-4.018932	-0.573725
O	0.000000	0.000000	3.083551
C	0.000000	2.865950	-0.582147
O	0.000000	4.018932	-0.573725

3 MP2/6-311+G* singlet spin state, C_1, NImag=0
Etot = -567.009970; ZPE_CORR = -566.953516;
Gibbs free energy = -566.990390

C	1.546803	-0.590853	0.038718
C	0.683732	0.602524	-0.062482
C	0.631890	-1.702117	0.068537
C	-0.625856	-1.704495	0.068587
C	-1.544483	-0.596348	0.039190
C	-0.685022	0.599610	-0.063158
C	-0.003965	1.901617	-0.001401
C	-2.882870	-0.584866	-0.019093
O	-4.046461	-0.554133	-0.050342
O	-0.006428	3.094499	0.063390
C	2.885135	-0.577224	-0.019759
O	4.048865	-0.551251	-0.049903

3 UB3PW91/6-311+G*triplet spin state, C_{2v}, NImag=0
Etot = -568.228917; ZPE = -568.172902; TFE = -568.209997;
$\langle S^2 \rangle$ = 2.019

C	0.000000	0.678644	0.671748
C	0.000000	-0.678644	0.671748
C	0.000000	-1.452929	-0.548200
C	0.000000	-0.666564	-1.749463
C	0.000000	0.666564	-1.749463
C	0.000000	1.452929	-0.548200
C	0.000000	-2.802015	-0.580313
O	0.000000	-3.945391	-0.642192
C	0.000000	2.802015	-0.580313
O	0.000000	3.945391	-0.642192
C	0.000000	0.000000	1.943851
O	0.000000	0.000000	3.135838

4 B3PW91/6-311+G*, singlet spin state, D_{3h}, NImag=0
E = -568.207687; ZPE_CORR = -568.153203;
Gibbs free energy = -568.189615

C	1.309703	0.756158	0.000000
C	0.000000	1.326754	0.000000
C	1.149003	-0.663377	0.000000
C	0.000000	-1.512315	0.000000
C	-1.149003	-0.663377	0.000000
C	-1.309703	0.756158	0.000000
C	2.346732	-1.354886	0.000000
C	0.000000	2.709772	0.000000
C	-2.346732	-1.354886	0.000000
O	3.328616	-1.921778	0.000000
O	-3.328616	-1.921778	0.000000
O	0.000000	3.843555	0.000000

Single point **MP2/6-311+G*//B3PW91/6-311+G*** E = -566.943985338

4 MP2/6-311+G*, singlet spin state, D_{3h}, NImag=0
E = -566.945096; ZPE_CORR = -566.891704;
Gibbs free energy = -566.927874

C	1.309703	0.756158	0.000000
C	0.000000	1.326754	0.000000
C	1.149003	-0.663377	0.000000
C	0.000000	-1.512315	0.000000
C	-1.149003	-0.663377	0.000000
C	-1.309703	0.756158	0.000000
C	2.346732	-1.354886	0.000000
C	0.000000	2.709772	0.000000
C	-2.346732	-1.354886	0.000000
O	3.328616	-1.921778	0.000000
O	-3.328616	-1.921778	0.000000
O	0.000000	3.843555	0.000000

4 triplet spin state, C_1, NImag=0
E = -568.169185; ZPE_CORR = -568.115584;
Gibbs free energy = -568.155142;
$\langle S^2 \rangle$ = 2.038

C	0.814082	-1.252411	0.068387
C	1.473837	-0.001620	0.078306
C	-0.613636	-1.163314	0.017634
C	-1.445926	0.001222	-0.023886
C	-0.611483	1.164150	0.017593
C	0.816409	1.250458	0.068502
C	-1.433002	-2.256470	-0.014222
C	2.843289	-0.002170	-0.004484
C	-1.428997	2.258687	-0.014231
O	-2.144934	-3.153970	-0.030752
O	-2.139411	3.157396	-0.030728
O	3.973416	-0.002324	-0.083719