Supporting Information: Metamorphic meta isomer: carbon dioxide and ketenes are formed via retro-Diels–Alder reactions in the decomposition of meta-benzenediol

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Time of flight mass spectra

Figures S1 and S2 show time-of-flight mass spectra at 11.5 eV (Figure S1) and 14.1 eV (Figure S2). The nature of the species in Figure S1 is discussed in the paper. The m/z 15 peak is assigned to the methyl radical (*vide infra*). The peak at m/z 30 corresponds to ethane. However, the signal was independent of the pyrolysis temperature, and we conclude that it was a contamination present in the experimental chamber.



Figure S1. Time-of-flight mass spectra at a photon energy of 11.5 eV at different pyrolysis temperatures. For better readability certain peaks are individually labelled. A thorough discussion of the spectra can be found in the main text.



Figure S2. Time-of-flight mass spectra at a photon energy of 14.1 eV at different pyrolysis temperatures. Only the m/z 20–50 range is pictured. New, higher IE species observed here are CO (m/z 28), O_2 (m/z 32, signal of residual atmosphere in the experimental chamber), and CO₂ (m/z 44). The appearance of m/z 38 and 37 may be associated with dissociative ionization of C₃H₃, which is known to appear at photon energies between 12.5 – 13 eV.¹

Mass-selected threshold photoelectron spectra (ms-TPES)

Figures S3–5 show photoion mass-selected threshold photoelectron spectra for the observed species. Assignment was carried out by comparison to literature spectra when available or FC calculated spectra otherwise. Although the assignment but-2-yne (m/z 54), and the penta-1,3-diynyl radical (m/z 63) is inconclusive, this is extraneous to the paper.

Figure S5 shows the ms-TPES for m/z 82, which formally corresponds to the product of the first CO loss and was postulated to have the structure of cyclopentadiene with an OH group substituting a hydrogen.² Unfortunately, definite assignment was not possible. Several different isomers may be formed and they may also quickly interconvert. Additionally, we expect very broad bands due to the rotation of the hydroxy group for these molecules.



Figure S3. Photoion mass-selected threshold photoelectron spectra. Along with the measured spectra either a simulated or a literature spectrum is shown to identify the structure.³⁻⁷ The band at aroud 8 eV in the ms-TPE spectrum of m/z 40 is due to some leakage of higher order radiation and following threshold ionization. The small peak at 8.7 eV is assigned to the ¹³C isotope of the propargyl radical.



Figure S4. Mass-selected threshold photoelectron spectra. Along with the measured spectra either a simulated or a literature spectrum is shown to identify the structure.^{4, 8-10}



Figure S5. Mass-selected threshold photoelectron spectra of m/z 82. Due to the lack of features no assignement could be carried out.

Theoretical studies and results

Name	Structure	IE (G4) [eV]	IE (exp.) [eV]
Penta-1,2,4-triene	≫ ~~″	8.62	/
Penta-1,2,4-triene	< <u> </u>	8.70	8.76
Ethynylcyclopropane		9.11	/
Penta-1,2,3-triene	\=C=C=	8.67	/
[1.1.1]Propellane	¥	9.77	/
Pent-1-en-3-yne		8.97	/
<i>(E)</i> -Pent-3-en-1-yne	\langle	9.03	9.08
<i>(Z)</i> -Pent-3-en-1-yne		9.07	9.08
<i>(E)</i> -Pent-1-en-4-yne		9.79	/
(Z)-Pent-1-en-4-yne		9.81	9.80
2-Methylbut-1-en-3-yne	=-≪	9.20	9.21
3-Methylenecyclobut-1-ene		8.83	/
Cyclopentadiene		8.57	8.57
Penta-1,3-diynyl radical	$\stackrel{H}{\rightarrow} = = H$	8.19	8.20
Buta-1,3-dienal	C [∞]	8.38	8.41

Table S1: Summary of G4-calculated AIEs in this work. If available, experimental AIEs are also given.

Name	Structure	Energy relative to Resorcinol [eV]
TS1	OH OH OH	2.86
11	ощ	0.69
TS2	o=	3.05
12	°=↓ Ô	0.43
TS3		3.25
13		0.65
TS4	,o	3.00
2 + CO ₂		1.29
TS5	C H	3.23
TS6	H	4.42
3 + CO ₂		1.18
5+ CO ₂		1.39
TS7 + CO ₂		3.36
15 + CO ₂		3.39

Table S2: Summary of the transition state (TS) and intermediate (I) structures along with energies relative to resorcinol for Figure 4 and 5 of the main article. Calculations were performed at G4 level of theory.

Name	Structure	Energy relative to Resorcinol [eV]
TS8 + CO ₂	H, C	3.86
TS9 + CO ₂		3.48
14 + CO ₂	C :	2.73
TS10 + CO ₂	CC H	3.09
1 + CO ₂		0.01
6 + CO ₂ + H		3.48
TS11 + CO ₂	H H H H H H H H H H H H H H H H H H H	4.23
TS12 + CO ₂		4.25
7 + HCCH + CO ₂		2.78
8 + HCHH + CO ₂		2.83
TS13		3.05
16		0.76
TS14		3.18

Name	Structure	Energy relative to Resorcinol [eV]
TS15		3.32
9 + 10		2.48
TS16	н, , , , , , , , , , , , , , , , , , ,	2.87
17	. С.	2.86
TS17	ОН	2.91
18	ОН	2.22
TS18	OH OH	3.33
19	С	2.14
TS19	ОН	2.76
11 + CO	ОН	1.50



Figure S6. Reaction mechanism for alternative CO loss which forms cyclopenta-1,4-dien-1-ol.

References

- 1. T. Schüßler, W. Roth, T. Gerber, C. Alcaraz and I. Fischer, *Phys. Chem. Chem. Phys.*, 2005, 7, 819-825.
- 2. A. M. Scheer, C. Mukarakate, D. J. Robichaud, M. R. Nimlos, H.-H. Carstensen and G. B. Ellison, 2012, 136, 044309.
- 3. B. K. Cunha de Miranda, C. Alcaraz, M. Elhanine, B. Noller, P. Hemberger, I. Fischer, G. A. Garcia, H. Soldi-Lose, B. Gans, L. A. Mendes, S. Boye-Peronne, S. Douin, J. Zabka and P. Botschwina, *J. Phys. Chem. A*, 2010, 114, 4818-4830.
- 4. P. Hemberger, G. da Silva, A. J. Trevitt, T. Gerber and A. Bodi, *Phys. Chem. Chem. Phys.*, 2015, 17, 30076-30083.
- D. Felsmann, K. Moshammer, J. Kruger, A. Lackner, A. Brockhinke, T. Kasper, T. Bierkandt, E. Akyildiz, N. Hansen, A. Lucassen, P. Osswald, M. Kohler, G. A. Garcia, L. Nahon, P. Hemberger, A. Bodi, T. Gerber and K. Kohse-Hoinghaus, *Proc. Combust. Inst.*, 2015, 35, 779-786.
- 6. F. Brogli, E. Heilbronner, V. Hornung and E. Kloster-Jensen, Helv. Chim. Acta, 1973, 56, 2171-2178.
- 7. F. Brogli, E. Heilbronner, J. Wirz, E. Kloster-Jensen, R. G. Bergman, K. P. C. Vollhardt and A. J. Ashe, Helv. Chim. Acta, 1975, 58, 2620-2645.
- 8. A. Bodi, P. Hemberger, D. L. Osborn and B. Sztaray, J Phys Chem Lett, 2013, 4, 2948-2952.
- 9. P. Forster, J. P. Maier and F. Thommen, Chem. Phys., 1981, 59, 85-90.
- 10. T. K. Ormond, P. Hemberger, T. P. Troy, M. Ahmed, J. F. Stanton and G. B. Ellison, *Mol. Phys.*, 2015, 113, 2350-2358.