

# Supporting Information

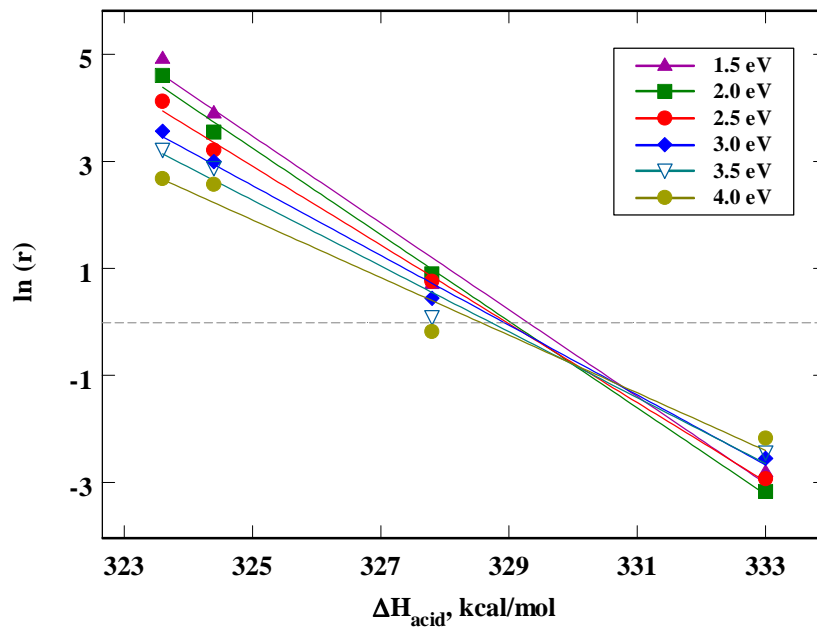
## Is the 1,3,5-*tris*(dehydro)benzene Triradical a Cyclopropenyl Radical Analogue?

Harvey A. Lardin, John J. Nash, and Paul G. Wenthold\*

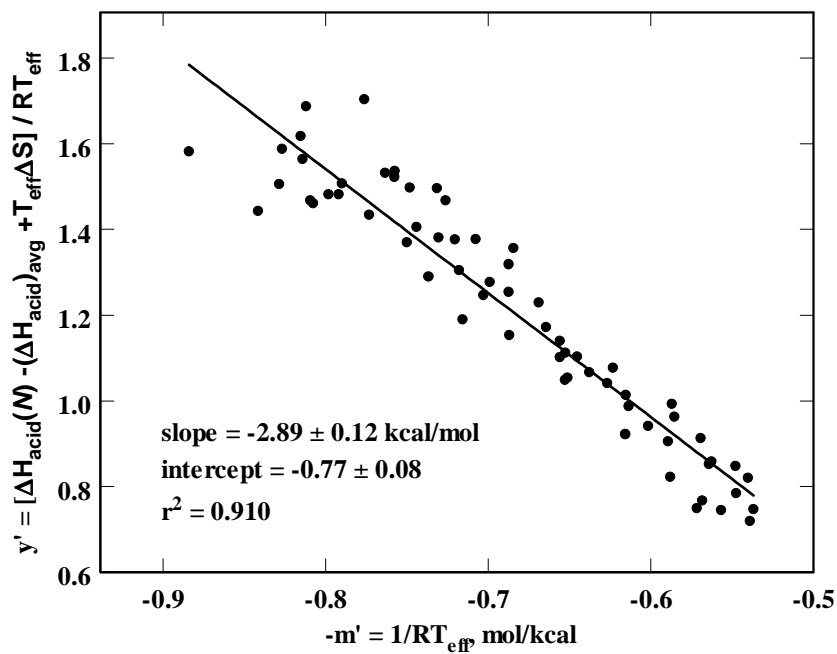
**Table S1.** Slopes and intercepts for first regression calibration curves in the kinetic method measurement of  $\Delta H_{\text{acid}}$  of 3,5-dichlorobenzoic acid.

Energy (eV)	Slope (kcal/mol)	Intercept	Energy (eV)	Slope (kcal/mol)	Intercept
1.48	-0.81	1.69	2.76	-0.69	1.25
1.52	-0.88	1.58	2.80	-0.69	1.15
1.56	-0.79	1.51	2.84	-0.67	1.23
1.60	-0.84	1.44	2.88	-0.66	1.14
1.64	-0.82	1.62	2.92	-0.66	1.17
1.68	-0.78	1.70	2.96	-0.66	1.10
1.72	-0.83	1.59	3.00	-0.65	1.11
1.76	-0.81	1.56	3.04	-0.65	1.05
1.80	-0.83	1.51	3.08	-0.65	1.10
1.84	-0.79	1.48	3.12	-0.65	1.05
1.88	-0.81	1.46	3.16	-0.64	1.07
1.92	-0.77	1.43	3.20	-0.63	1.04
1.96	-0.76	1.54	3.24	-0.62	1.08
2.00	-0.81	1.47	3.28	-0.61	0.99
2.04	-0.76	1.53	3.32	-0.62	1.01
2.08	-0.80	1.48	3.36	-0.59	0.99
2.12	-0.75	1.37	3.40	-0.60	0.94
2.16	-0.76	1.52	3.44	-0.59	0.96
2.20	-0.74	1.41	3.48	-0.62	0.92
2.24	-0.75	1.50	3.52	-0.59	0.91
2.28	-0.71	1.38	3.56	-0.57	0.91
2.32	-0.73	1.47	3.60	-0.59	0.82
2.36	-0.73	1.50	3.64	-0.56	0.85
2.40	-0.73	1.38	3.68	-0.56	0.86
2.44	-0.72	1.30	3.72	-0.57	0.77
2.48	-0.74	1.29	3.76	-0.55	0.85
2.52	-0.72	1.38	3.80	-0.54	0.82
2.56	-0.69	1.32	3.84	-0.57	0.75
2.60	-0.68	1.36	3.88	-0.55	0.78
2.64	-0.70	1.25	3.92	-0.56	0.75
2.68	-0.70	1.28	3.96	-0.54	0.75
2.72	-0.72	1.19	4.00	-0.54	0.72

**Figure S1.** First regression plots of  $\ln(r)$  vs.  $\Delta H_{\text{acid}}$  at 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 eV (c.m.) for calibration sets used in the kinetic method measurement of  $\Delta H_{\text{acid}}$ (3,5-dichlorobenzoic acid).



**Figure S2.** Second regression plot of  $[\Delta H_{\text{acid}}(7) - (\Delta H_{\text{acid}})_{\text{avg}} + T_{\text{eff}} \delta\Delta S]/RT_{\text{eff}}$  vs.  $-1/RT_{\text{eff}}$  for the kinetic method measurement of  $\Delta H_{\text{acid}}$  of 3,5-dichlorobenzoic acid.

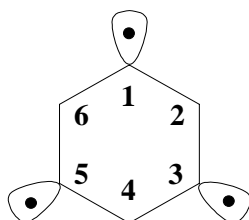


**Table S2.** Slopes and intercepts for first regression calibration curves in the kinetic method measurement of the EA of 5-chloro-*m*-benzyne.

<b>Energy (eV)</b>	<b>Slope (kcal/mol)</b>	<b>Intercept</b>	<b>Energy (eV)</b>	<b>Slope (kcal/mol)</b>	<b>Intercept</b>
<b>3.32</b>	-15.74	1.03	<b>5.72</b>	-12.25	0.80
<b>3.38</b>	-15.07	1.15	<b>5.78</b>	-12.57	0.84
<b>3.44</b>	-14.90	0.96	<b>5.84</b>	-13.28	0.99
<b>3.50</b>	-14.62	1.03	<b>5.90</b>	-12.64	0.99
<b>3.56</b>	-13.48	1.05	<b>5.96</b>	-12.92	0.99
<b>3.62</b>	-13.70	0.88	<b>6.02</b>	-13.56	1.08
<b>3.68</b>	-13.81	0.78	<b>6.08</b>	-12.38	0.96
<b>3.74</b>	-13.29	1.09	<b>6.14</b>	-12.66	1.04
<b>3.80</b>	-13.47	0.91	<b>6.20</b>	-12.46	0.79
<b>3.86</b>	-13.92	1.29	<b>6.26</b>	-12.03	0.85
<b>3.92</b>	-15.63	1.30	<b>6.32</b>	-12.13	1.12
<b>3.98</b>	-13.52	1.08	<b>6.38</b>	-13.01	0.93
<b>4.04</b>	-13.18	1.09	<b>6.44</b>	-12.62	1.05
<b>4.10</b>	-12.53	0.69	<b>6.50</b>	-12.28	0.79
<b>4.16</b>	-13.32	1.06	<b>6.56</b>	-12.04	0.80
<b>4.22</b>	-13.82	0.99	<b>6.62</b>	-12.36	0.88
<b>4.28</b>	-15.23	1.39	<b>6.68</b>	-12.60	0.77
<b>4.34</b>	-14.24	1.09	<b>6.74</b>	-12.81	0.97
<b>4.40</b>	-13.56	1.09	<b>6.80</b>	-11.86	0.81
<b>4.46</b>	-13.90	1.20	<b>6.86</b>	-11.50	0.85
<b>4.52</b>	-13.59	0.93	<b>6.92</b>	-12.20	0.73
<b>4.58</b>	-13.42	0.89	<b>6.98</b>	-12.18	0.92
<b>4.64</b>	-14.18	1.16	<b>7.04</b>	-11.93	0.82
<b>4.70</b>	-12.53	1.17	<b>7.10</b>	-12.07	0.73
<b>4.76</b>	-12.69	1.00	<b>7.16</b>	-12.13	0.96
<b>4.82</b>	-12.51	0.93	<b>7.22</b>	-12.00	0.91
<b>4.88</b>	-13.20	1.12	<b>7.28</b>	-11.80	0.71
<b>4.94</b>	-12.77	0.88	<b>7.34</b>	-11.12	0.74
<b>5.00</b>	-13.30	0.84	<b>7.40</b>	-11.89	0.77
<b>5.06</b>	-13.55	1.01	<b>7.46</b>	-11.94	0.65
<b>5.12</b>	-13.30	1.04	<b>7.52</b>	-11.41	0.93
<b>5.18</b>	-13.20	1.17	<b>7.58</b>	-11.26	0.56
<b>5.24</b>	-13.86	1.16	<b>7.64</b>	-11.73	0.73
<b>5.30</b>	-13.13	1.17	<b>7.70</b>	-11.53	0.78
<b>5.36</b>	-13.67	0.92	<b>7.76</b>	-11.66	0.67
<b>5.42</b>	-13.88	1.05	<b>7.82</b>	-12.03	0.73
<b>5.48</b>	-12.25	1.09	<b>7.88</b>	-11.52	0.80
<b>5.54</b>	-12.24	0.97	<b>7.94</b>	-11.49	0.67
<b>5.60</b>	-12.78	1.05	<b>8.00</b>	-11.83	0.70
<b>5.66</b>	-13.48	1.14			

**Table S3.** C-C bond lengths,  $r$ , and C-C-C bond angles,  $a$ , for 1,3,5-*tris*(dehydro)benzene. Bond lengths are in Å, and bond angles are in degrees.

Species	$r_{C1-C2}$	$r_{C2-C3}$	$r_{C3-C4}$	$a_{C1-C2-C3}$	$a_{C2-C3-C4}$	$a_{C3-C4-C5}$	$a_{C6-C1-C2}$
<b>MCSCF(9,9)/3-21G</b>							
( $C_{2v}$ Symmetry)							
$^2A_1$ state	1.3928	1.3875	1.3896	115.84	128.88	109.10	121.46
$^2B_2$ state	1.3852	1.3958	1.3893	111.97	124.19	117.38	130.31
$^4B_2$ state	1.3909	1.3917	1.3908	116.38	128.62	116.39	123.63
<b>BLYP/aug-cc-pVDZ</b>							
( $C_{2v}$ Symmetry)							
$^2A_1$ state	1.4149	1.3807	1.3784	112.79	139.91	96.09	118.52
$^2B_2$ state	1.3698	1.4123	1.3983	105.22	125.57	117.03	141.41
$^4B_2$ state	1.3979	1.3979	1.3979	115.22	124.79	115.21	124.77



**Table S4.** Vibrational frequencies for 1,3,5-*tris*(dehydro)benzene ( $^2A_1$ ,  $^2B_2$  and  $^4B_2$  electronic states) calculated at the BLYP/aug-cc-pVDZ level of theory. Values are in  $cm^{-1}$ .

$^2A_1$ Electronic State		$^2B_2$ Electronic State		$^4B_2$ Electronic State	
397.1980	1051.6433	-254.9054	1042.6284	132.5794	1016.4557
407.6070	1162.3691	440.2906	1177.6224	134.7796	1160.6698
440.8100	1184.5347	463.4981	1202.0100	571.2481	1274.2871
500.2185	1272.1020	506.0129	1222.0622	594.3731	1300.9713
504.0036	1296.0181	556.0302	1338.7338	594.5920	1301.3743
681.4806	1444.9571	722.4210	1421.3519	740.6678	1489.6089
778.9103	1644.5673	731.8736	1613.0605	741.2667	1489.8356
781.4166	3132.6602	793.0725	3112.9929	750.8644	3071.9856
785.5988	3134.1149	816.2403	3150.3175	943.7091	3072.1483
949.9622	3139.4362	964.6621	3153.4908	994.2969	3076.3325
1013.8196		1005.0053		1015.9949	

**Table S5.** CASPT2/cc-pVDZ electronic energies for three low lying electronic states of 1,3,5-*tris*(dehydro)benzene and for species used in calculating Triradical Stabilization Energies (TSEs). The geometries used for these energy calculations are indicated in Table S6 for the triradical or in Ref. 69. Zero-point vibrational energies and thermal corrections to enthalpy for each species were calculated at the BLYP/aug-cc-pVDZ//BLYP/aug-cc-pVDZ level of theory.

Species	Electronic Energy	ZPE	Thermal Correction (H <sub>298</sub> – H <sub>0</sub> )
<b>1,3,5-<i>tris</i>(dehydro)benzene</b>			
<sup>2</sup> A <sub>1</sub> state	-229.54054	0.058557	0.064216
<sup>2</sup> B <sub>2</sub> state	-229.54002	0.057941	0.063187
<sup>4</sup> B <sub>2</sub> state	-229.49907	0.058020	0.064150
<b><i>meta</i>-Benzyne</b>			
<sup>1</sup> A <sub>1</sub> state	-230.21082	0.071008	0.076670
<sup>3</sup> B <sub>2</sub> state	-230.18363	0.071439	0.076953
<b>Phenyl Radical</b>	-230.86278	0.084185	0.089669
<b>Benzene</b>	-231.53800	0.097083	0.102564