

Structural manifestations of the cheletropic reaction†

Goh Yit Wooi and Jonathan M. White*

School of Chemistry, The University of Melbourne, Parkville, VIC 3010, Melbourne, Australia

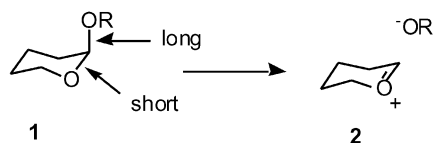
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Examination of selected cyclopentenone derivatives which are fixed into the boat conformation reveals structural deviations from 'normal' C–C(O) and C=O bond distances consistent with the early stages of the cheletropic extrusion of carbon monoxide.

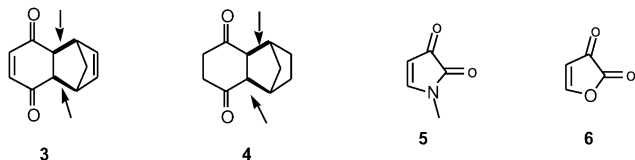
Introduction

Structural changes which occur along a reaction coordinate can appear in the ground state of the reactant as measurable deviations of bond distances and angles from 'normal values' along the reaction coordinate and are believed to represent the early stages of the reaction.¹ This is the structure-correlation principle and it applies when the molecule in question exists in a ground state geometry, which is similar to the transition state geometry for the reaction. A classic example of this principle is provided by the series of structures of 2-oxygenated derivatives of tetrahydropyran **1** (Scheme 1).² The structures are characterised by short endocyclic C–O bonds, and long exocyclic C–OR bonds, consistent with progress along the reaction coordinate towards the oxonium ion **2**.



Scheme 1

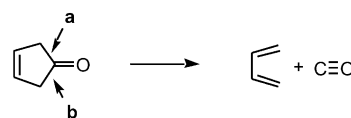
Thermal pericyclic fragmentation reactions such as the *retro* Diels–Alder reaction are ideal candidates for study using the structure-correlation principle; the precursor molecules can be readily prepared, and readily constrained into the reactive boat conformation. For example, in the benzoquinone cycloadduct **3** the carbon-carbon bonds which break in the *retro* Diels–Alder reaction are lengthened by *ca.* 0.03 Å compared to the corresponding saturated adduct **4** which cannot undergo the *retro* Diels–Alder reaction.^{3,4}



Recently, structural effects consistent with the onset of the planar pseudopericyclic decarbonylation⁵ have been observed in molecules containing the pyrroledione **5** and furandione **6** substructures.⁶

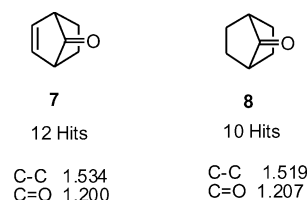
We were interested to determine whether the structural changes associated with the thermal cheletropic decarbonylation of cyclopentenones⁷ would appear in the ground state (Scheme 2). These effects include lengthening of bonds **a** and **b** which are broken in the reaction and smaller effects on the remaining C–C bond distances and the C=O bond distance.

† Electronic supplementary information (ESI) available: Summary of the CCD search results for fragments **7** and **8**. See <http://www.rsc.org/suppdata/ob/b4/b417538g/>

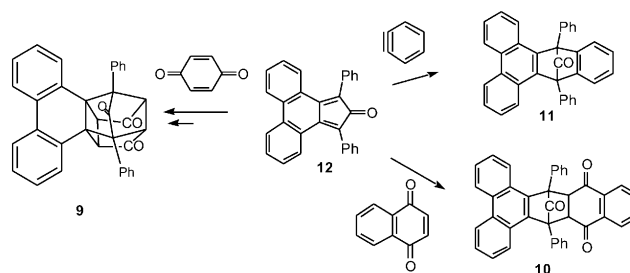


Scheme 2

The cheletropic decarbonylation of cyclopentenones is a disrotatory process,^{7,8} thus a ground state geometry which most closely resembles the transition state for this reaction can be achieved in the bicyclic fragment **7**. A survey of the Cambridge Crystallographic Database⁹ for molecules containing the bicyclic cyclopentenone fragment **7** (which are potential substrates for the thermal cheletropic extrusion of carbon monoxide) was carried out. For comparison purposes the saturated bicyclic fragment **8** which cannot undergo this reaction was also extracted from the CSD. Only those structures with R factors <5% and with esd values on the C–C distances between 0.001 and 0.005 Å were retained. This small set of structures shows that the C–C bonds which break during the cheletropic loss of CO in **7** are indeed longer than in the corresponding fragment **8** which cannot undergo this reaction, furthermore there is a slight decrease in the C=O bond which develops some triple-bond character during the reaction.



To further examine the structural features associated with the cheletropic reaction we prepared and determined the low temperature crystal structures of the three cycloadducts **9**, **10**, and **11** (Scheme 3).‡ Compound **9**, an adduct of the cyclopentadienone **12** and benzoquinone, undergoes a further [2+2] cycloaddition during crystallisation, this process occurred in dull light. This compound cannot formally undergo the cheletropic reaction and is therefore ideal for comparison purposes. Compounds **10** and **11** can both undergo cheletropic decarbonylation, however decarbonylation of **11** generates a new aromatic ring and has been reported to occur cleanly at relatively low temperatures.¹⁰



Scheme 3

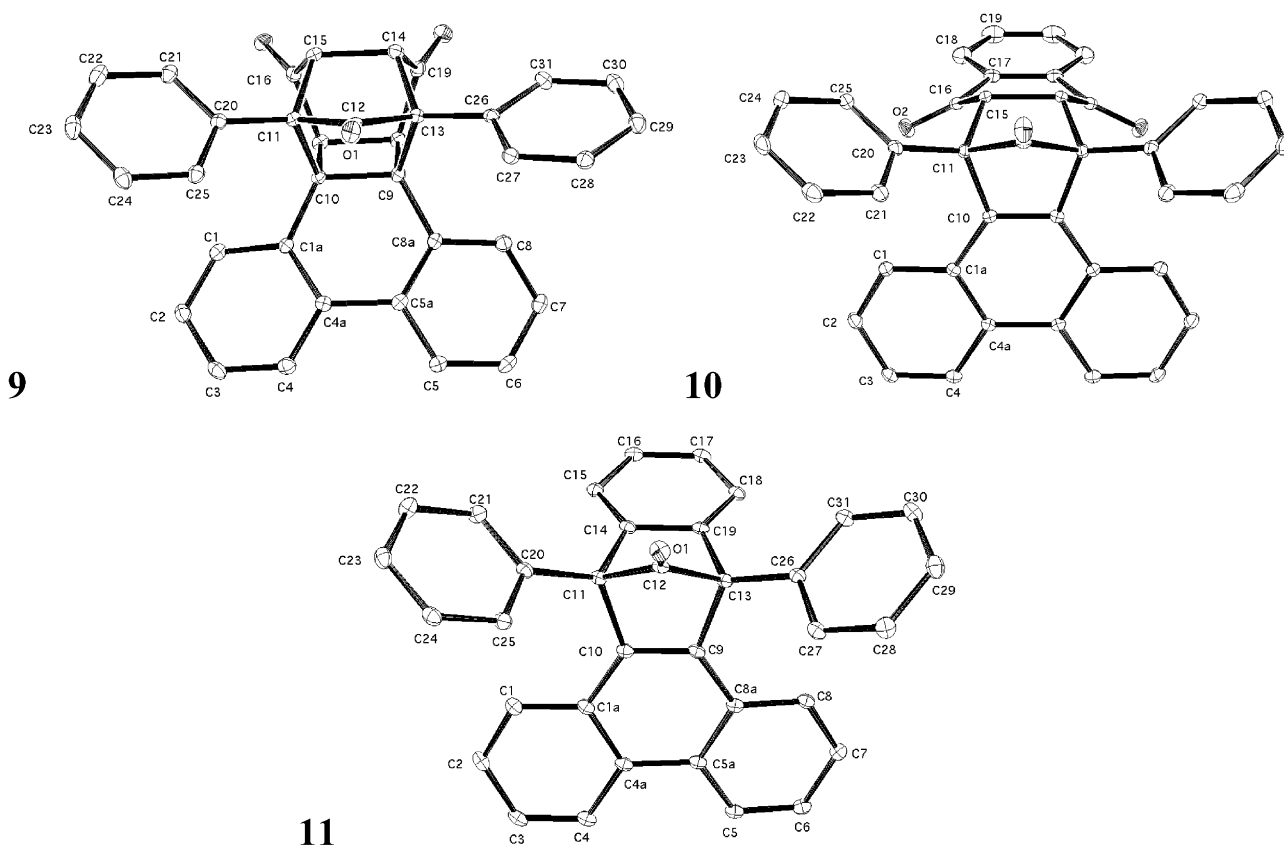


Fig. 1 Thermal ellipsoid plots for compounds 9–11.

Thermal ellipsoid plots for 9–11 are presented in Fig. 1 and relevant structural parameters are presented in Table 1.

Compound **10** lies on a crystallographic plane of symmetry while **9** and **11** show good agreement between bond distances and angles related by an approximate non-crystallographic plane of symmetry. The mean C–C(O) bond distances in **9** (which cannot undergo cheletropic decarbonylation) are 1.530(3) Å. The corresponding distance in the reactive benzyne adduct **11** is 1.559(2) Å which is significantly lengthened. The mean C–C(O) distance in the less reactive adduct **10** is 1.541(2) which is intermediate between these two values. The C=O bond distances in **10** and **11** are slightly shorter than in **9**, consistent with the development of some triple bond character; it is interesting to note that the infrared stretching frequencies (ν_{\max}) for **10** and **11**, which are 1796 and 1806 cm^{-1} , respectively, differ significantly from **9** (1755 cm^{-1}), also indicating some triple bond character.

These results clearly demonstrate that the cheletropic decarbonylation does manifest in the ground state as measurable deviations of bond distances along the reaction coordinate. Furthermore a qualitative relationship between structure and reactivity has been established.

Experimental

General experimental procedures have been published previously.¹¹

Table 1 Selected structural parameters for compounds 9–11

	9	10	11
C12–O1	1.204(2) Å	1.194(2) Å	1.197(2) Å
C11–C12	1.533(3) Å	1.541(2) Å	1.557(2) Å
C12–C13	1.528(3) Å	1.541(2) Å	1.560(2) Å
C9–C13–C14	100.1(2)°	107.0(1)°	104.4(1)°
C10–C11–C15	100.3(2)°	107.0(1)°	103.9(1)°
C–C(O)–C	101.1(2)°	100.6(1)°	99.5(1)°

Phencyclone 12

Phenanthrene-9,10-quinone (0.75 g, 3.6 mmol) was added to 1,3-diphenyl-2-propanone (0.80 g, 3.8 mmol) in dry methanol (45 ml) in a two-necked round bottom flask fitted with a water-cooled condenser and a dropping funnel containing a solution of methanolic potassium hydroxide (0.2 g KOH in 0.8 ml) in dry methanol. The reaction mixture was stirred while heating. The methanolic potassium hydroxide solution was added dropwise once the methanol began to reflux. The reaction was further refluxed for 15 min. The black powder formed upon chilling was filtered and washed with cold methanol, dried on vacuum to yield the product (1.20 g, 87%), mp 226–228 °C; IR (KBr) 1700 (C=O); ^1H NMR (CDCl_3) δ 6.92 (t, 2H), 7.24 (d, 2H), 7.35–7.43 (m, 10H), 7.53 (d, 2H), 7.78 (d, 2H); ^{13}C NMR (CDCl_3) δ 123.1, 124.4, 128.1, 128.2, 128.4, 128.6, 129.0, 129.9, 131.4, 132.2, 133.5, 148.2, 200.2.

Phencyclone benzoquinone cycloadduct 9

Phencyclone (0.38 g, 1.0 mmol) in 10 ml dry benzene was added to benzoquinone (0.16 g, 1.5 mmol) in 10 ml dry benzene. The reaction was stirred at 80 °C until the reaction mixture change from black to bright yellow. The solvent was removed under vacuum. Recrystallisation from chloroform yielded a pale yellow powder. (0.40 g, 82%) Recrystallisation from benzene–ethanol gave very fine yellowish block crystals, mp 279–282 °C (darken at 245 °C and shrink at 257 °C). IR (KBr) 1679, 1791 (C=O); ^1H NMR (CDCl_3) δ 4.60 (s, 2H), 5.75 (s, 2H), 7.08 (d, 2H), 7.18 (d, 2H), 7.25 (t, 2H), 7.34 (t, 2H), 7.46 (t, 2H), 7.56 (t, 2H), 7.66 (t, 2H), 8.27 (d, 2H), 8.68 (d, 2H); ^{13}C NMR (CDCl_3) δ 48.1, 65.5, 123.22, 126.0, 126.3, 126.7, 127.2, 128.2, 128.3, 128.9, 131.2, 133.2, 134.0, 140.8, 141.5, 194.7, 198.1. Attempted recrystallisation by dissolving the yellowish powder in minimum amount of ethyl acetate, with heating and under the exposure of sunlight, led to the formation of the fully saturated cycloadduct

9 as colourless blocks, mp 335–338 °C (darken at 333 °C); ν_{\max} (KBr) 1755 (C=O); ^1H NMR (CDCl_3) δ 3.29 (d, 2H), 3.81 (d, 2H), 5.66 (d, 2H), 6.66 (t, 2H), 6.88 (broad s, 2H), 7.16–7.28 (m, 10H), 7.86 (d, 2H); ^{13}C NMR (CDCl_3) δ 51.3, 51.9, 54.1, 61.1, 122.8, 127.3, 128.0, 128.6, 129.4, 129.5, 130.1, 131.3, 204.7, 208.1.

Phencyclone napthaquinone cycloadduct 10

Phencyclone (0.38 g, 1.0 mmol) in 10 ml dry benzene was added to napthaquinone (0.16 g, 1.5 mmol) in 10 ml dry benzene. The reaction was stirred at 80 °C until the reaction mixture changed from black to bright orange. The solvent was removed under vacuum and the residue was recrystallised from chloroform to give orange block crystals (0.46 g, 85%), mp 253–255 °C; ν_{\max} (KBr) 1691, 1796 (C=O); ^1H NMR (CDCl_3) δ 4.80 (s, 2H), 6.66–6.76 (m, 4H), 6.98 (s, 2H), 7.13–7.78 (m, 10H), 8.08–8.11 (m, 2H), 8.34 (d, 2H), 8.46 (d, 2H); ^{13}C NMR (CDCl_3) δ 49.1, 65.6, 122.8, 124.4, 125.6, 126.4, 126.7, 126.9, 128.1, 128.4, 129.1, 130.7, 131.2, 132.3, 133.5, 134.0, 136.3, 194.6, 198.5.

Phencyclone benzyne cycloadduct 11

Phencyclone (0.50 g, 1.3 mmol) was dissolved in 1,2-dichloroethane (20 ml) in a three-necked round bottom flask which was fitted with two dropping funnel and a water cooled condenser. Anthranilic acid (0.18 g, 1.3 mmol) in 15 ml 1,2-dichloroethane was placed in one of the dropping funnels and the other was charged with isoamyl nitrile (0.35 ml, 2.6 mmol) in 15 ml of 1,2-dichloroethane. The reaction mixture was heated to reflux and solutions from the dropping funnels were simultaneously added dropwise to the refluxing mixture over a period of 20 min. After the addition was completed, the dark green solution changed to pale yellow. The mixture was further refluxed for 60 min and solvent was removed under reduced pressure. The residue was recrystallised from acetonitrile to give colorless block crystals (0.52 g, 90%). Air bubbles were observed to evolve from the product at 93–95 °C during the mp determination, and they left behind a white compound which melted at 285–289 °C. ν_{\max} (KBr) 1806 (C=O); ^1H NMR (CDCl_3) δ 8.71 (d, 2H), 7.21–8.15 (m, 20H); ^{13}C NMR (CDCl_3) δ 66.8, 123.5, 125.8, 126.0, 126.1, 126.5, 126.9, 127.8, 128.5, 130.4, 132.0, 132.5, 142.1, 144.6, 195.0.

X-ray crystallography†

Crystal data for 9. $\text{C}_{35}\text{H}_{22}\text{O}_3$, $M = 490.53$, triclinic, P-1, $a = 10.0236(11)$, $b = 10.4368(11)$, $c = 12.1152(13)$ Å, $V = 1155.4(2)$ Å³, $a = 109.755(2)^\circ$, $\beta = 103.475(2)^\circ$, $\gamma = 90.167(2)^\circ$, $Z = 2$, $D_{\text{calc}} = 1.410 \text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.089 \text{ mm}^{-1}$, 6182 reflections measured ($2\theta_{\max} = 25^\circ$), 4034 unique ($R_{\text{int}} = 0.0390$), 2534 having $I > 2\sigma(I)$. Full matrix least squares on F^2 , $R1 = 0.0456$, $wR2 =$

0.0676, GOF = 0.803, max. and min. difference peak and hole 0.189 and -0.185 e Å^{-3} , respectively.

Crystal data for 10. $\text{C}_{39}\text{H}_{24}\text{O}_3$, $M = 540.58$, Hexagonal, $P6(3)/m$, $a = 15.3580(4)$, $b = 15.3580(4)$, $c = 20.1237(12)$ Å, $V = 4110.6(3)$ Å³, $Z = 6$, $D_{\text{calc}} = 1.310 \text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.082 \text{ mm}^{-1}$, 25909 XXX measured ($2\theta_{\max} = 27.5^\circ$), 3233 unique ($R_{\text{int}} = 0.098$), 1982 having $I > 2\sigma(I)$. Full matrix least squares on F^2 , $R1 = 0.0497$, $wR2 = 0.0772$, GOF = 0.887, max. and min. difference peak and hole 0.24 and -0.21 e Å^{-3} , respectively.

Crystal data for 11. $\text{C}_{35}\text{H}_{22}\text{O}_{1.5}(\text{CH}_3\text{CN})_{1.5}$, $M = 520.11$, monoclinic, $C2/c$, $a = 20.7668(18)$, $b = 10.7728(8)$, $c = 25.1640(18)$ Å, $\beta = 104.376(2)^\circ$, $V = 5453.3(7)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.267 \text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.076 \text{ mm}^{-1}$, 14041 measured ($2\theta_{\max} = 25.0^\circ$), 4789 unique ($R_{\text{int}} = 0.094$), 4195 having $I > 2\sigma(I)$. Full matrix least squares on F^2 , $R1 = 0.0481$, $wR2 = 0.1329$, GOF = 1.072, max. and min. difference peak and hole 0.30 and -0.22 e Å^{-3} , respectively.

Intensity data were collected with a Bruker SMART Apex CCD detector using Mo K α radiation (graphite crystal monochromator $\lambda = 0.71073$). Data were reduced using the program SAINT.¹² The structure was solved by direct methods and difference Fourier synthesis.

Acknowledgements

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Notes and references

† CCDC reference numbers 256554–256556. See <http://www.rsc.org/suppdata/ob/b4/b417538g/> for crystallographic data in .cif format.

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