Carbon Dioxide Entrapment in an Organic Molecular Host

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1. Materials and Methods

4-Phenoxyphenol was purchased from Sigma-Aldrich. Thermogravimetric analysis were performed on Perkin Elmer TGA 7 using a 10 °C.min^{-1} heating rate under a nitrogen atmosphere with a 50 ml.min^{-1} flow rate. X-ray powder diffraction experiments were carried out on a PanAlytical instrument using Cu-Kα radiation (λ = 1.5418 Å). Attenuated total reflection infrared spectroscopy (ATR-IR) was carried out on a Thermo Nicolet instrument using the Smart Golden Gate ATR attachment.

2. Single-Crystal X-Ray Diffraction

Intensity data were collected on a Bruker DUO CCD diffractometer using graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å). The temperature of the crystals was controlled using an Oxford Cryostream Cooler. Data reduction was carried out by means of a standard procedure using the APEX II software. Where necessary, systematic errors in the intensity data were corrected for using SADABS. The structures were solved by direct methods using SHELXS-97.[1] All atoms were located by this method. All ordered non-hydrogen atoms were refined anisotropically by means of full-matrix least squares calculations on F^2 using SHELXL-97[1] within the X-Seed[2] environment. Where appropriate, hydrogen atoms were placed in calculated positions using riding models and assigned isotropic thermal parameters 1.2 times those of their parent atoms for aromatic C. All phenol hydrogen atoms were located in the difference electron density maps and their isotropic thermal parameters were refined freely. Molecular graphics were produced using the program POV-Ray.[3]

Crystal data for **2·vac·293K**: $C_{12}H_{10}O_2$, M = 186.20, colourless rod, 0.40 × 0.20 × 0.20 mm^3, trigonal, space group R-3 (No. 148), $a = b$ = 29.2571(16), c = 5.9378(3) Å, V = 4401.7(4) Å^3, Z = 18, D_c = 1.264 g/cm^3, F_{000} = 1764, Bruker Duo CCD Area Detector, MoKα radiation, λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 64.6º, 22590 reflections collected, 3483 unique (R$_{int}$ = 0.0418). Final $GooF$ = 0.999, $R1$ = 0.0506, $wR2$ = 0.1192, R indices based on 2001 reflections with I >2sigma(I) (refinement on F^2), 131 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.086 mm^{-1}.

Crystal data for **2·vac·100K**: $C_{12}H_{10}O_2$, M = 186.20, colourless rod, 0.40 × 0.20 × 0.20 mm^3, trigonal, space group R-3 (No. 148), $a = b$ = 29.0785(18), c = 5.8540(4) Å, V = 4286.7(5) Å^3, Z = 18, D_c = 1.298 g/cm^3, F_{000} = 1764, Bruker Duo CCD Area Detector, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 67.7º, 22841 reflections collected, 3691 unique (R$_{int}$ =

0.0351). Final $GooF$ = 1.035, $R1$ = 0.0430, $wR2$ = 0.1092, R indices based on 2923 reflections with I >2sigma(I) (refinement on F^2), 131 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.088 mm^{-1}.

Crystal data for **2·36%CO$_2$**: $C_{12.05}H_{10}O_{2.11}$, M = 188.55, colourless needle, 0.40 × 0.10 × 0.10 mm^3, trigonal, space group R-3 (No. 148), a = b = 29.000(4), c = 5.8505(8) Å, V = 4260.9(10) Å^3, Z = 18, D_c = 1.323 g/cm^3, F_{000} = 1785, Bruker Duo CCD Area Detector, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 54.9º, 10595 reflections collected, 2149 unique (R_{int} = 0.1032). Final $GooF$ = 1.026, $R1$ = 0.0522, $wR2$ = 0.1072, R indices based on 1303 reflections with I >2sigma(I) (refinement on F^2), 136 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.090 mm^{-1}.

Crystal data for **2·73%CO$_2$**: $C_{12.12}H_{10}O_{2.24}$, M = 191.55, colourless needle, 0.40 × 0.10 × 0.10 mm^3, trigonal, space group R-3 (No. 148), a = b = 28.906(10), c = 5.862(2) Å, V = 4242(3) Å^3, Z = 18, D_c = 1.350 g/cm^3, F_{000} = 1812, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 55.1º, 15769 reflections collected, 2172 unique (R_{int} = 0.0961). Final $GooF$ = 1.014, $R1$ = 0.0500, $wR2$ = 0.1255, R indices based on 1407 reflections with I >2sigma(I) (refinement on F^2), 137 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.093 mm^{-1}.

Crystal data for **2·CO$_2$**: $C_{12.17}H_{10}O_{2.33}$, M = 193.53, colourless needle, 0.40 × 0.08 × 0.08 mm^3, trigonal, space group R-3 (No. 148), a = b = 28.908(6), c = 5.8899(12) Å, V = 4262.6(15) Å^3, Z = 18, D_c = 1.357 g/cm^3, F_{000} = 1830, Bruker Duo CCD Area Detector, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 56.5º, 16014 reflections collected, 2294 unique (R_{int} = 0.0435). Final $GooF$ = 1.032, $R1$ = 0.0393, $wR2$ = 0.1012, R indices based on 1820 reflections with I >2sigma(I) (refinement on F^2), 136 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.094 mm^{-1}.
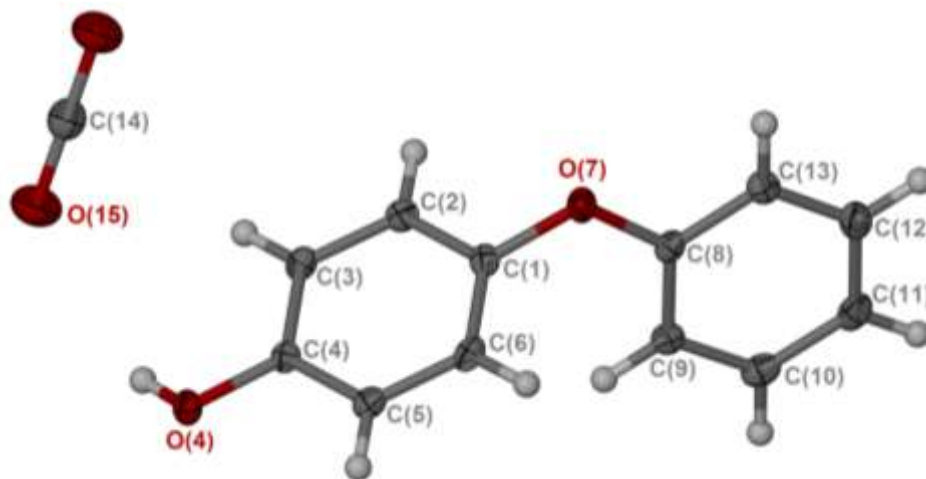

Fig. S1 Thermal ellipsoid plot of **2·CO$_2$** shown at 50% probability. The asymmetric unit is labelled.
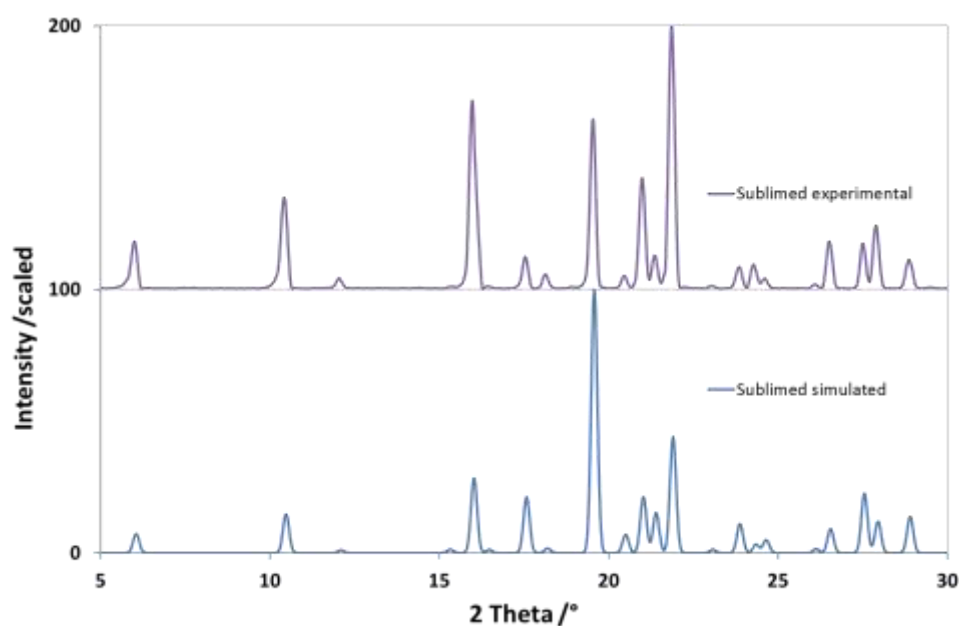
3. Powder X-Ray Diffraction

Fig. S2 A comparison of the powder pattern of sublimed **2** used for gas sorption experiments and a pattern simulated from **2·vac·293K**.

4. Gravimetric Gas Sorption

Gravimetric sorption isotherms were measured using an Intelligent Gravimetric Analyser (IGA-002) supplied by Hiden Analytical (Ltd), Warrington, UK.[4] Only ultra-high purity gasses were used. The pressure is monitored using a pressure transducer with a range of 0-20 bar and buoyancy effects are corrected for automatically by the control software. Temperature control is maintained to an accuracy of +/- 0.05 K using a Grant refrigerated recirculating bath.
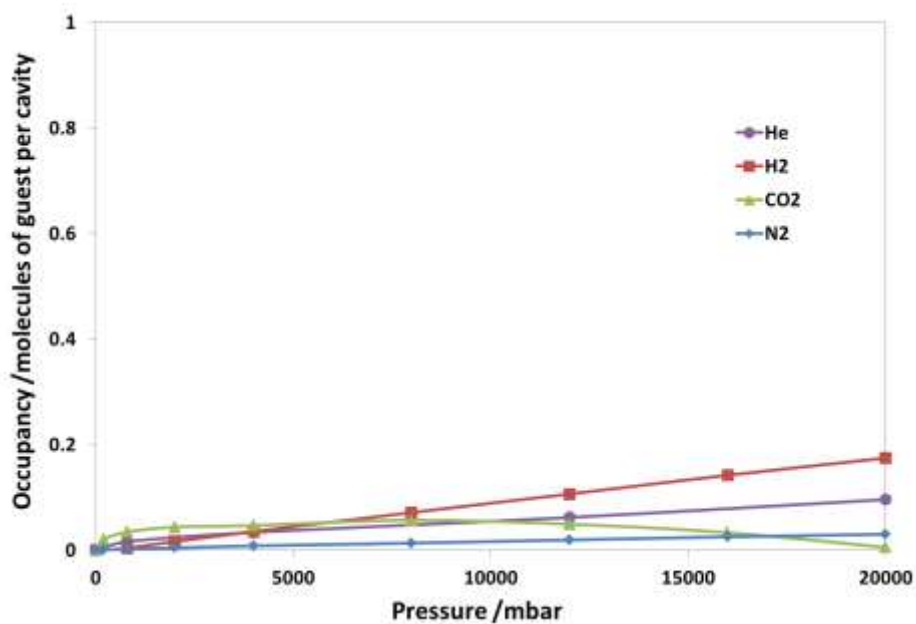

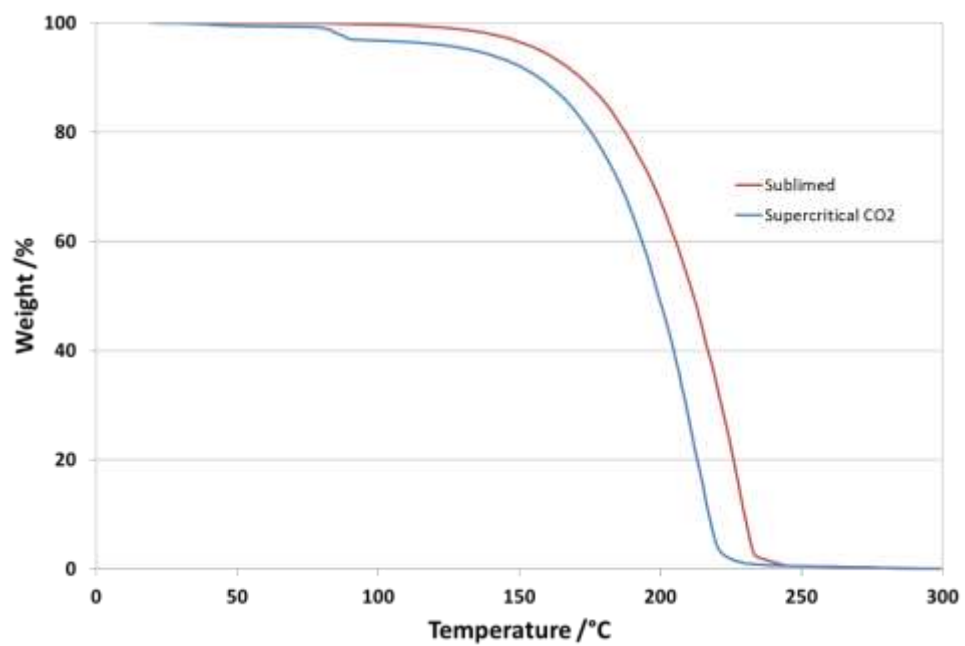**Fig. S3** Gas sorption isotherms at 293 K.

5. Thermal Analysis

Fig. S4 Thermogravimetric analysis of sublimed **2** and **2·CO₂** grown from supercritical CO_2.
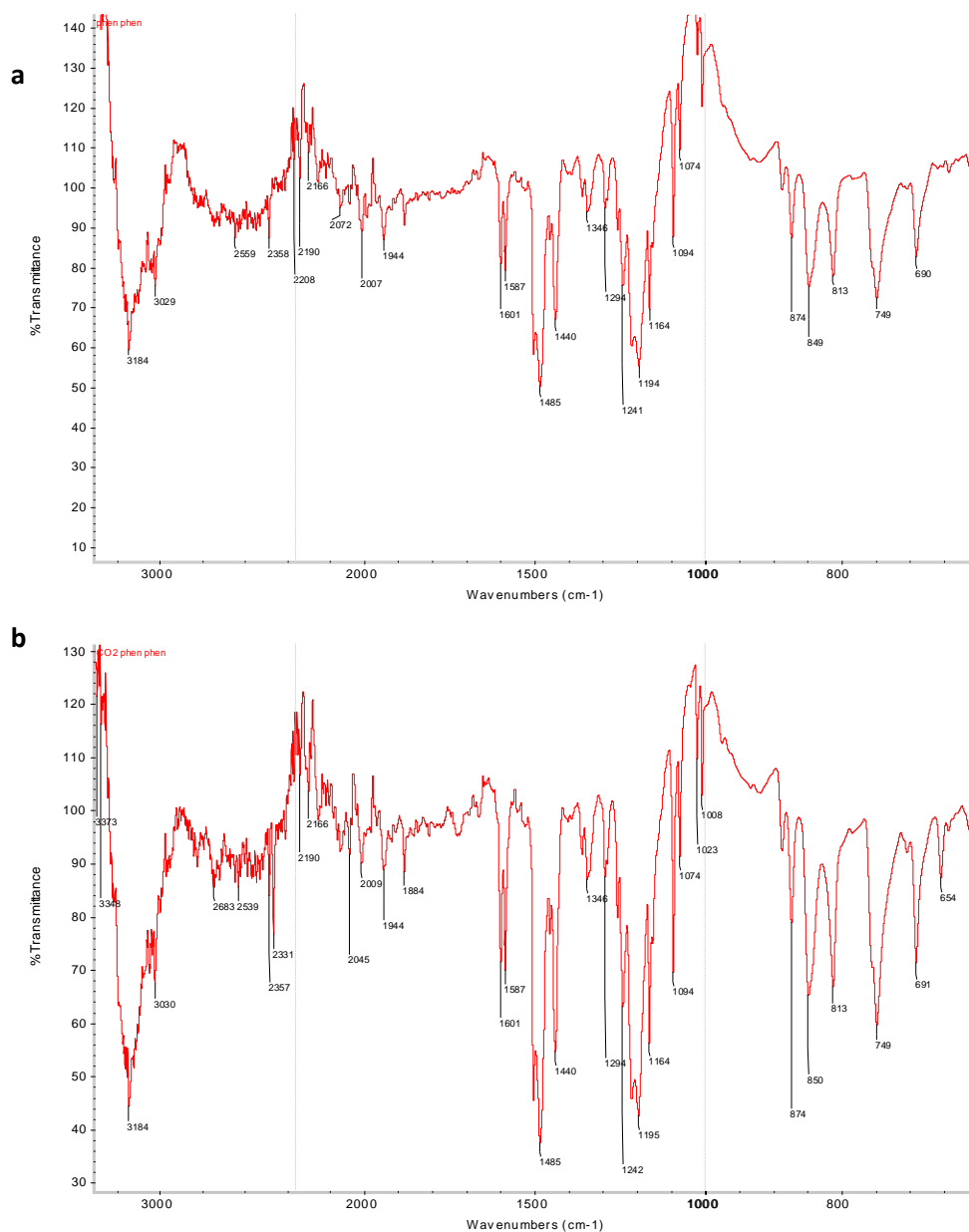
6. Infrared Spectroscopy

Fig. S5 ATR-IR spectrum of (a) sublimed **2** and (b) **2·CO₂**. A sharp absorption band is seen at 2331 cm^{-1} for the CO_2 asymmetric stretch, and a band can be seen at 654 cm^{-1} for the CO_2 bending[5].

7. References

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