Table S1: Crystallographic data for bianthrone at increasing pressures.

Pressure/ GPa	Ambient	1.2	2.2	3.3
Formula	$C_{28}O_2H_{16}$	$C_{28}O_2H_{16}$	$C_{28}O_2H_{16}$	$C_{28}O_2H_{16}$
M_r	384.43	384.43	384.43	384.43
Cell setting, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a, *b*, *c* (Å)	10.1860 (3), 8.4277 (2), 11.6457 (3)	9.9825 (11), 7.8892 (15), 11.4879 (9)	9.9021 (14), 7.6543 (18), 11.4225 (11)	9.8354 (13), 7.4567 (19), 11.3543 (12)
β (°)	109.591 (2)	109.780 (6)	109.860 (9)	109.939 (8)
V (Å)	941.85 (4)	851.3 (2)	814.3 (2)	782.8 (2)
Z	2	2	2	2
D_x (Mg m^{-3})	1.355	1.500	1.568	1.631
μ (mm^{-1})	0.08	0.09	0.10	0.10
Crystal form, colour	Block, Yellow	Block, Yellow	Block, Yellow	Block, Yellow
Crystal size (mm)	0.57 × 0.33 × 0.31	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
T_{min}	0.82	0.86	0.78	0.84
T_{max}	0.97	0.99	0.99	0.99
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections.	12386, 2349, 1867	4044, 852, 644	3792, 818, 625	3798, 772, 583
R_{int}	0.049	0.087	0.087	0.093
d_{max}, d_{min}/ Å	8.84, 0.75	6.14, 0.90	8.63, 0.90	6.04, 0.90
Refinement on	*F*	*F*	*F*	*F*
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.055, 0.051, 1.11	0.045, 0.044, 1.01	0.044, 0.047, 1.04	0.042, 0.043, 1.04
No. of parameters	136	136	136	136
Weighting Scheme	Chebychev polynomial (Prince, 1982) (Watkin, 1994)	Chebychev polynomial (Prince, 1982) (Watkin, 1994)	Chebychev polynomial (Prince, 1982) (Watkin, 1994)	Chebychev polynomial (Prince, 1982) (Watkin, 1994)
$(?/s)_{max}$	<0.0001	<0.0001	<0.0001	<0.0001
$??_{max}$, $??_{min}$ (e Å^{-3})	0.24, –0.19	0.12, –0.13	0.14 –0.15	0.15, –0.16
Completeness	99.8% (0.75 Å)	69.2% (0.9 Å)	68.7% (0.9 Å)	69.6% (0.9 Å)

Table S1: *Continued*

Pressure/ GPa	4.2	5.1	6.0	6.5
Formula	$C_{28}O_2H_{16}$	$C_{28}O_2H_{16}$	$C_{28}O_2H_{16}$	$C_{28}O_2H_{16}$
M_r	384.43	384.43	384.43	384.43
Cell setting, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a, *b*, *c* (Å)	9.7854 (7), 7.2988 (11), 11.3074 (7)	9.7527 (9), 7.2058 (15), 11.2786 (9)	9.7286 (10), 7.1123 (17), 11.2468 (11)	9.7119 (14), 7.041 (2), 11.2282 (18)
β (°)	110.028 (4)	110.132 (6)	110.186 (7)	110.229 (10)
V (Å)	758.75 (14)	744.19 (18)	730.4 (2)	720.4 (3)
Z	2	2	2	2
D_x (Mg m^{-3})	1.683	1.716	1.748	1.772
μ (mm^{-1})	0.11	0.11	0.11	0.11
Crystal form, colour	Block, Yellow	Block, Yellow	Block, Yellow	Block, Yellow
Crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
T_{min}	0.84	0.79	0.76	0.81
T_{max}	0.99	0.99	0.99	0.99
No. of measured, independent and observed [$I > 2.0s(I)$] reflections.	3269, 689, 554	3280, 649, 506	3365, 623, 487	3016, 641, 473
R_{int}	0.074	0.093	0.081	0.117
d_{max}, d_{min}/ Å	4.64, 0.90	5.98, 0.90	5.96, 0.90	5.95, 0.90
Refinement on	*F*	*F*	*F*	*F*
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, *S*	0.042, 0.044, 1.07	0.041, 0.047, 1.08	0.041 0.029 1.09	0.051, 0.039, 1.09
No. of parameters	136	136	136	136
Weighting Scheme	Chebychev polynomial (Prince, 1982) (Watkin, 1994)	Chebychev polynomial (Prince, 1982) (Watkin, 1994)	Chebychev polynomial (Prince, 1982) (Watkin, 1994)	Chebychev polynomial (Prince, 1982) (Watkin, 1994)
$(? / s)_{max}$	<0.0001	<0.0001	<0.0001	<0.0001
$? ?_{max}$, $? ?_{min}$ (e Å^{-3})	0.16, –0.16	0.12, –0.12	0.14, –0.15	0.19, –0.19
Completeness	65.7% (0.9 Å)	65.1% (0.9 Å)	62.4% (0.9 Å)	67.3% (0.9 Å)

Table S2: The main non-covalent interactions for the crystal structure of bianthrone with increasing pressure. Distances are in Å and angles are given in º. S.u's are calculated in PLATON. Interactions involving rings are measured from the centroid of the ring. Hydrogen distances are not normalised to standard neutron values.

Pressure (GPa)	**0**	**1.2**	**2.2**	**3.3**
Interaction #1 (Inter-layer)				
C11H6...O1[i]				
H6…O1	2.59	2.40	2.35	2.32
C11…O1	3.309(2)	3.055(3)	2.962(3)	2.898(4)
<C11H6O1	133	126	122	119
C10H5...R1[i]				
H5…R2	3.75	3.66	3.61	3.59
C10…R2	4.624(3)	4.525(4)	4.474(4)	4.441
<C10H5R2	155	153	153	150
R2…R1 [ii]				
R2...R1	4.367(1)	4.088(2)	3.964(2)	3.855(2)
Offset	2.114	1.905	1.794	1.677
C4H2...R3 [iii]				
H2…R3	3.07	2.88	2.82	2.77
C4…R3	3.489(3)	3.255(4)	3.162(4)	3.082(4)
<C4H2R3	108	105	103	100
Energy (kJmol^{-1})	-34.7	-33.3	-30.4	-23.6
Interaction #2 (Intra-layer)				
C5H3...R3[iv]				
H3…R3	3.51	3.42	3.35	3.29
C5…R3	4.450(3)	4.236(4)	4.157(4)	4.093(4)
<C5H3R3	146	145	144	144
Energy (kJmol^{-1})	-18.4	-18.2	-17.4	-16.4
Interaction #3 (Inter-layer)				
C12H7...R3[v]				
H7…R3	3.45	3.17	3.03	2.92
C12…R3	4.090(3)	3.791(4)	3.650(4)	3.536(4)
<C12H7R3	127	124	124	124
C6H4…H7C12[vi]				
H4…H7	2.52	2.30	2.21	2.14
Energy (kJmol^{-1})	-17.0	-18.0	-19.2	-19.1
Interaction #4 (Intra-layer)				
C13H8...O1[vii]				
H8…O1	2.49	2.40	2.35	2.32
C13…O1	3.396(2)	3.256(3)	3.186(3)	3.132(3)
<C13H8O1	159	150	147	143
Energy (kJmol^{-1})	-15.1	-14.0	-14.5	-14.5
Interaction #5 (Intra-layer)				
C3H1…H1C3 [viii]				
H1…H1	2.72	2.41	2.29	2.19
C4H2…H1C3 [viii]				
H2…H1	2.89	2.78	2.72	2.65
Energy (kJmol^{-1})	-10.3	-12.6	-13.7	-13.7

Pressure (GPa)	4.2	5.1	6.0	6.5
Interaction #1 (Inter-layer)				
C11H6...O1[i]				
H6…O1	2.29	2.27	2.26	2.23
C11…O1	2.840(3)	2.812(4)	2.784(4)	2.750(5)
<C11H6O1	116	116	114	113
C10H5...R1[i]				
H5…R2	3.56	3.55	3.53	3.53
C10…R2	4.411(4)	4.391(4)	4.373(4)	4.363(5)
<C10H5R2	150	149	149	148
R2…R1 [ii]				
R2...R1	3.775(2)	3.725(2)	3.678(2)	3.642(3)
Offset	1.590	1.515	1.448	1.345
C4H2...R3 [iii]				
H2…R3	2.73	2.75	2.71	2.70
C4…R3	3.027(4)	3.005(4)	2.972(4)	2.950(5)
<C4H2R3	99	96	97	96
Energy (kJmol^{-1})	-19.4	-15.6	-9.4	-3.5
Interaction #2 (Intra-layer)				
C5H3...R3[iv]				
H3…R3	3.25	3.22	3.20	3.18
C5…R3	4.046(4)	4.018(4)	3.996(5)	3.976(5)
<C5H3R3	143	143	143	143
Energy (kJmol^{-1})	-14.7	-13.6	-10.9	-9.5
Interaction #3 (Inter-layer)				
C12H7...R3[v]				
H7…R3	2.84	2.80	2.74	2.70
C12…R3	3.454(4)	3.406(4)	3.348(4)	3.312(5)
<C12H7R3	123	123	123	123
C6H4…H7C12[vi]				
H4…H7	2.09	2.06	2.03	2.01
Energy (kJmol^{-1})	-18.0	-17.4	-16.2	-14.7
Interaction #4 (Intra-layer)				
C13H8...O1[vii]				
H8…O1	2.29	2.28	2.27	2.25
C13…O1	3.077(3)	3.054(3)	3.029(3)	3.006(4)
<C13H8O1	140	138	137	136
Energy (kJmol^{-1})	-13.8	-13.0	-12.4	-11.0
Interaction #5 (Intra-layer)				
C3H1…H1C3 [viii]				
H1…H1	2.10	2.05	1.99	1.96
C4H2…H1C3 [viii]				
H2…H1	2.59	2.56	2.52	2.49
Energy (kJmol^{-1})	-13.6	-13.9	-13.9	-12.9

Symmetry Operators:

i	1/2+*x*, 1/2-*y*, 1/2+*z*
ii	3/2-*x*, 1/2+*y*, 1/2-*z*
iii	3/2-*x*, -1/2+*y*, 1/2-*z*
iv	-1+*x*, *y*, *z*
v	5/2-*x*, 1/2+*y*, 1/2-*z*
vi	1/2+*x*, 3/2-*y*, -1/2+*z*
vii	2-*x*, 1-*y*, -*z*
viii	1-*x*, 1-*y*, -*z*

Ring Identities:

R1	C2-C3-C4-C5-C6-C7
R2	C1-C2-C7-C8-C9-C14
R3	C9-C10-C11-C12-C13-C14

Table S3: Breakdown of the total interaction energy for each contact (#'s 1-5) featured in Figures 2 (a-c) and Table S2.

Energy Breakdown (kJmol^{-1})	0 GPa	1.2 GPa	2.2 GPa	3.3 GPa
Interaction #1				
E_{Coul}	-10.0	-20.1	-27.3	-34.8
E_{pol}	-5.3	-10.7	-14.6	-18.5
E_{disp}	-46.2	-65.3	-78.0	-86.4
E_{rep}	26.8	63.1	89.4	116.1
E_{tot}	-34.7	-33.0	-30.5	-23.6
Interaction #2				
E_{Coul}	-5.1	-10.4	-14.2	-18.0
E_{pol}	-2.6	-5.2	-7.6	-10.6
E_{disp}	-23.8	-33.6	-38.6	-42.6
E_{rep}	13.1	31.1	42.9	54.7
E_{tot}	-18.4	-18.2	-17.4	-16.4
Interaction #3				
E_{Coul}	-4.4	-7.8	-10.6	-13.1
E_{pol}	-2.7	-5.4	-7.9	-10.1
E_{disp}	-20.3	-28.3	-34.4	-39.5
E_{rep}	10.4	23.5	33.6	43.4
E_{tot}	-17.0	-18.0	-19.3	-19.2
Interaction #4				
E_{Coul}	-12.2	-15.4	-17.7	-19.1
E_{pol}	-5.4	-6.7	-8.2	-8.6
E_{disp}	-11.6	-13.3	-15.2	-16.8
E_{rep}	14.1	21.4	26.6	30.1
E_{tot}	-15.1	-14.0	-14.5	-14.5
Interaction #5				
E_{Coul}	-3.3	-5.0	-6.2	-7.7
E_{pol}	-0.9	-2.1	-3.3	-4.5
E_{disp}	-8.8	-12.4	-14.5	-16.5
E_{rep}	2.7	6.9	10.2	15.0
E_{tot}	-10.3	-12.6	-13.7	-13.7

Table S3: *Continued*

Energy Breakdown (kJmol^{-1})	4.2 GPa	5.1 GPa	6.0 GPa	6.5 GPa
Interaction #1				
E_{Coul}	-43.9	-48.8	-55.2	-60.4
E_{pol}	-23.5	-25.8	-29.6	-31.6
E_{disp}	-99.0	-104.6	-111.1	-115.4
E_{rep}	146.7	163.7	186.5	204.0
E_{tot}	-19.6	-15.6	-9.4	-3.5
Interaction #2				
E_{Coul}	-21.7	-23.5	-26.6	-28.4
E_{pol}	-14.3	-15.6	-17.4	-18.6
E_{disp}	-46.3	-48.7	-49.8	-51.0
E_{rep}	67.6	74.2	83.0	88.6
E_{tot}	-14.7	-13.6	-10.9	-9.5
Interaction #3				
E_{Coul}	-15.9	-17.9	-20.1	-22.0
E_{pol}	-12.5	-14.1	-16.2	-17.6
E_{disp}	-43.4	-46.3	-48.6	-50.4
E_{rep}	53.7	61.0	68.7	75.3
E_{tot}	-18.1	-17.4	-16.2	-14.7
Interaction #4				
E_{Coul}	-21.0	-21.5	-21.7	-22.3
E_{pol}	-9.7	-10.1	-10.5	-10.8
E_{disp}	-18.3	-18.8	-19.7	-20.3
E_{rep}	35.2	37.3	39.5	42.4
E_{tot}	-13.8	-13.0	-12.4	-11.0
Interaction #5				
E_{Coul}	-9.4	-10.7	-12.4	-13.9
E_{pol}	-6.2	-7.1	-8.9	-10.4
E_{disp}	-18.9	-20.7	-22.3	-23.0
E_{rep}	20.8	24.7	29.6	34.5
E_{tot}	-13.6	-13.9	-13.9	-12.9