Exploring The Excited-State Charge Transfer Fluorescence Profile of 7-Hydroxycoumarin and 2-Methylimidazole- A Combined X-Ray Diffraction and Theoretical Approach.

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Characterization of (1)

Diethylmalonate (3.15 g, 19.7 mmol) was added to a solution of 2,4-dihydroxybenzaldehyde (3 g, 21.6 mmol) in methanol (20 mL), followed by morpholine (163 μL, 1.87 mmol) and acetic acid (52 μL, 0.90 mmol) in methanol (1 mL). The reaction mixture was then refluxed, and, after completion by TLC, the mixture was allowed to cool to room temperature (25°C). The resulting solid was filtered, washed with methanol, and then recrystallised from methanol to give the final product as off-white solid plates (1.2 g, 24 %).
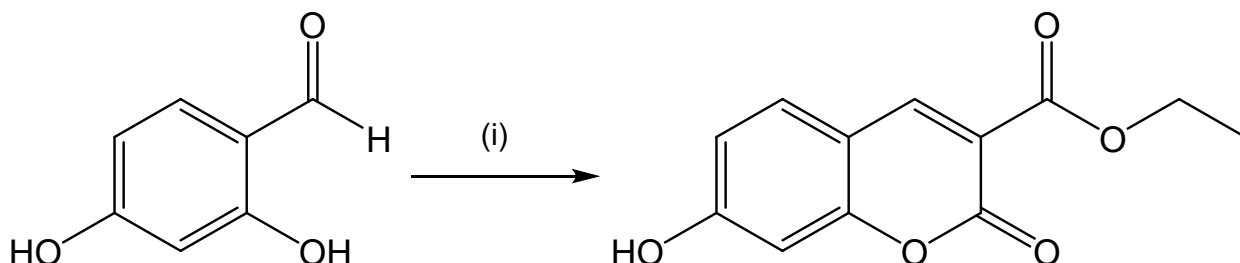
Scheme 1. Synthesis of ethyl 7-hydroxy-2-oxo-2H-chromene-3-carboxylate (**1**) *via* the Knoevenagel condensation of 2,4-dihydroxybenzaldehyde. Reaction conditions: (i) diethyl malonate, morpholine/acetic acid, MeOH, 85 °C, 3 h.
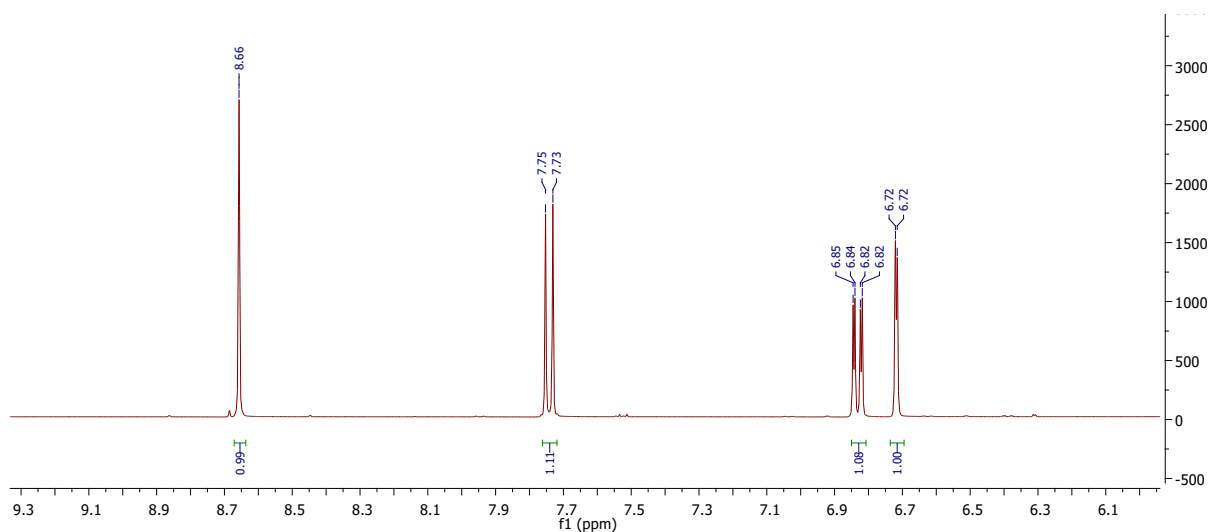
Figure S1. ^{1}H NMR spectrum of (1)

^{1}H NMR (400 MHz, DMSO-d_6) δ_H 1.29 (3H, t, J = 7.1 Hz, CH$_2$CH_3), 4.25 (2H, q, J = 7.1 Hz, CH_2CH$_3$), 6.72 (1H, d, J = 2.1 Hz, H-8), 6.83 (1H, dd, J = 8.6 Hz and 2.2 Hz, H-6), 7.74 (1H, d, J = 8.6 Hz, H-5), 8.66 (1H, s, H-4); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 14.15 (CH$_3$), 60.8 (CH$_2$), 101.8 (CH, C-8), 110.4 (quat, C-4a), 112.05 (quat, C-3), 114.05 (CH, C-6), 132.1 (CH, C-5), 149.4 (CH, C-4), 156.4 (C=O, C-2), 157.1 (quat, C-8a), 163.0 (ester C=O), 164.1 (quat, C-7); FTIR (neat, υ_{max}/cm^{-1}) 3545 (OH), 1734 (C=O), 1603 (C=C), 1225 (C-O); ESI-MS *m/z* 257 (MNa)$^+$.

Crystallographic Details

Collection, Data reduction and refinement

The X-Ray diffraction experiments were performed at the Sydney School of Pharmacy, Faculty of Medicine and Health, University of Sydney, NSW, Australia. The diffractions were performed on an Agilent SuperNova™ Dual Source System with a CCD Atlas detector. For (1), (2) and (3) a crystal sized 0.14 x 0.15 x 0.55 mm, 0.3 x 0.2 x 0.6 mm and 0.6 x 0.3 x 0.16 mm, respectively, were mounted on a thin glass fibre with multipurpose Paratone-N, acting as a cryoprotectant and adhesive throughout the collection. Data was collected using a $1°$ ω-scans with the detector distance fixed at 5in all data collections. The reciprocal space was covered by positioning the detector arm between 3.0(0) and 40.2(0) $°$, 3.2 (0) and 45.2(0) $°$, and 2.5(0) and 65.9(0) $°$ in 2θ for (1), (2) and (3), respectively. A total of 12124, 13019 and 58735 reflections were collected for (1), (2) and (3), respectively.

After collection, the data was sorted, scaled and merged using SORTAV by Blessing.[1] The final completenesses for (1), (2) and (3) were, 100%, 100% and 99.9%, respectively. The structures of (1), (2) and (3) were solved using direct methods (SHELXT), and a full-matrix least-squares refinement based on F^2 was performed using SHELXL-2015.[2] To confirm the reflection data for all systems was modelled appropriately *via* the independent atomic model, the residual densities were review to confirm each system had a gaussian distribution. The gaussian distribution infers that the model has accurately modelled the data collect, these models can be seen below Figure S2.

(a)

(b)

(c)
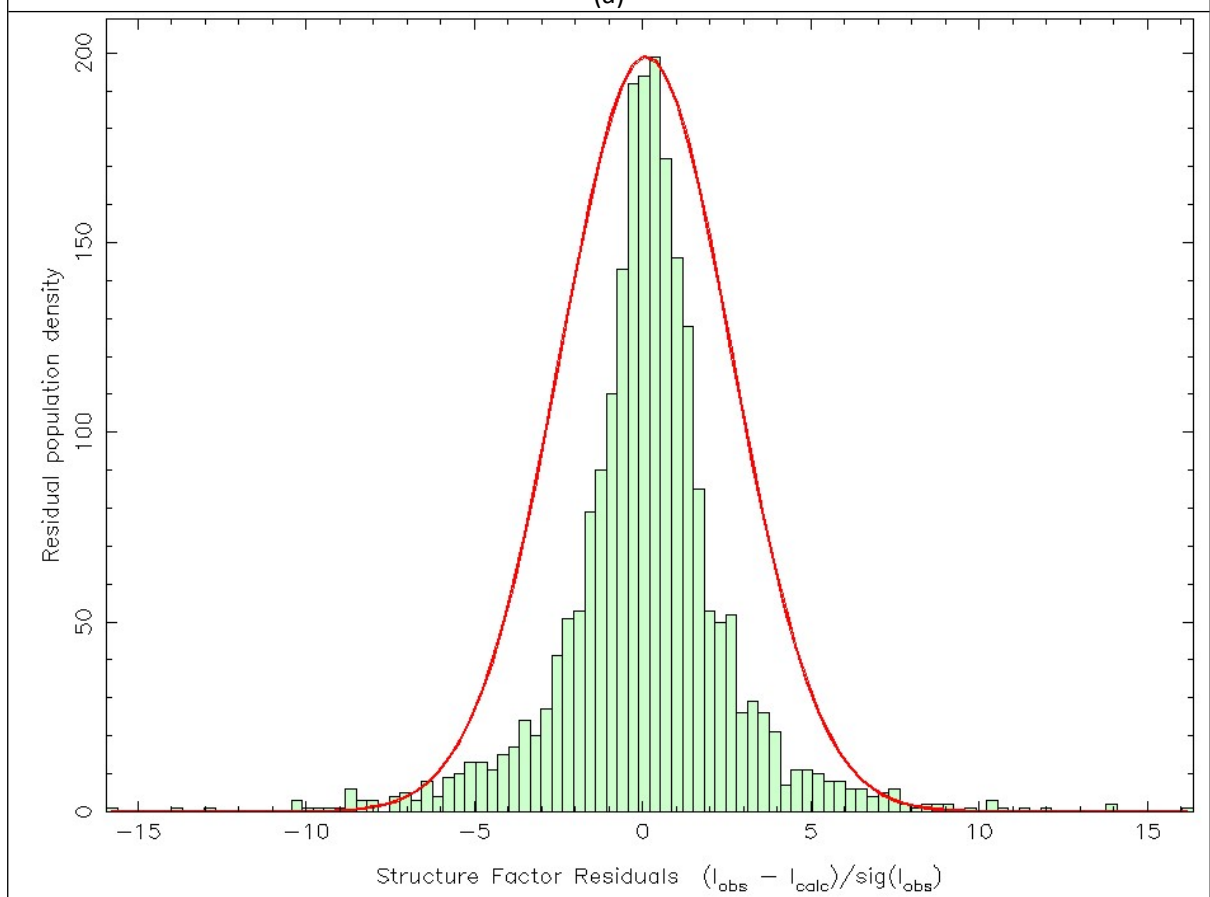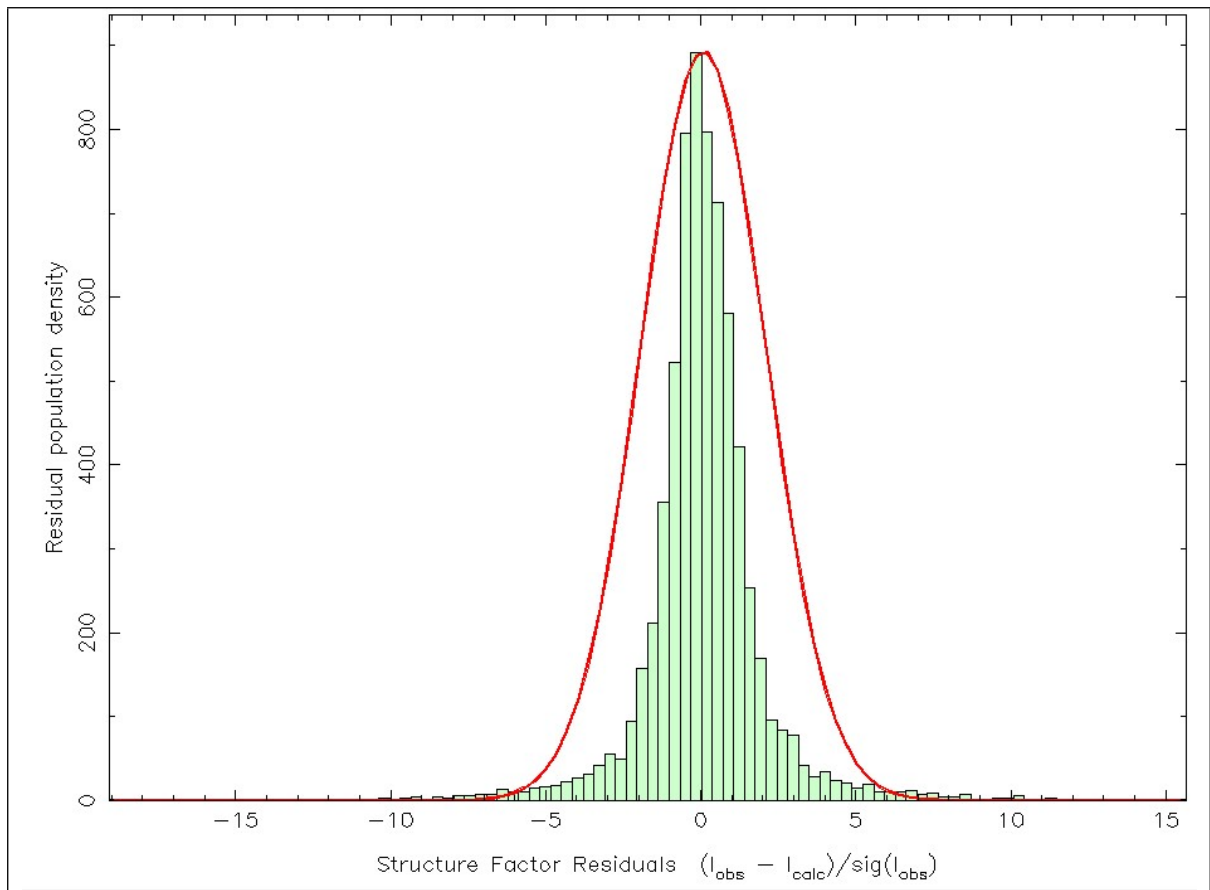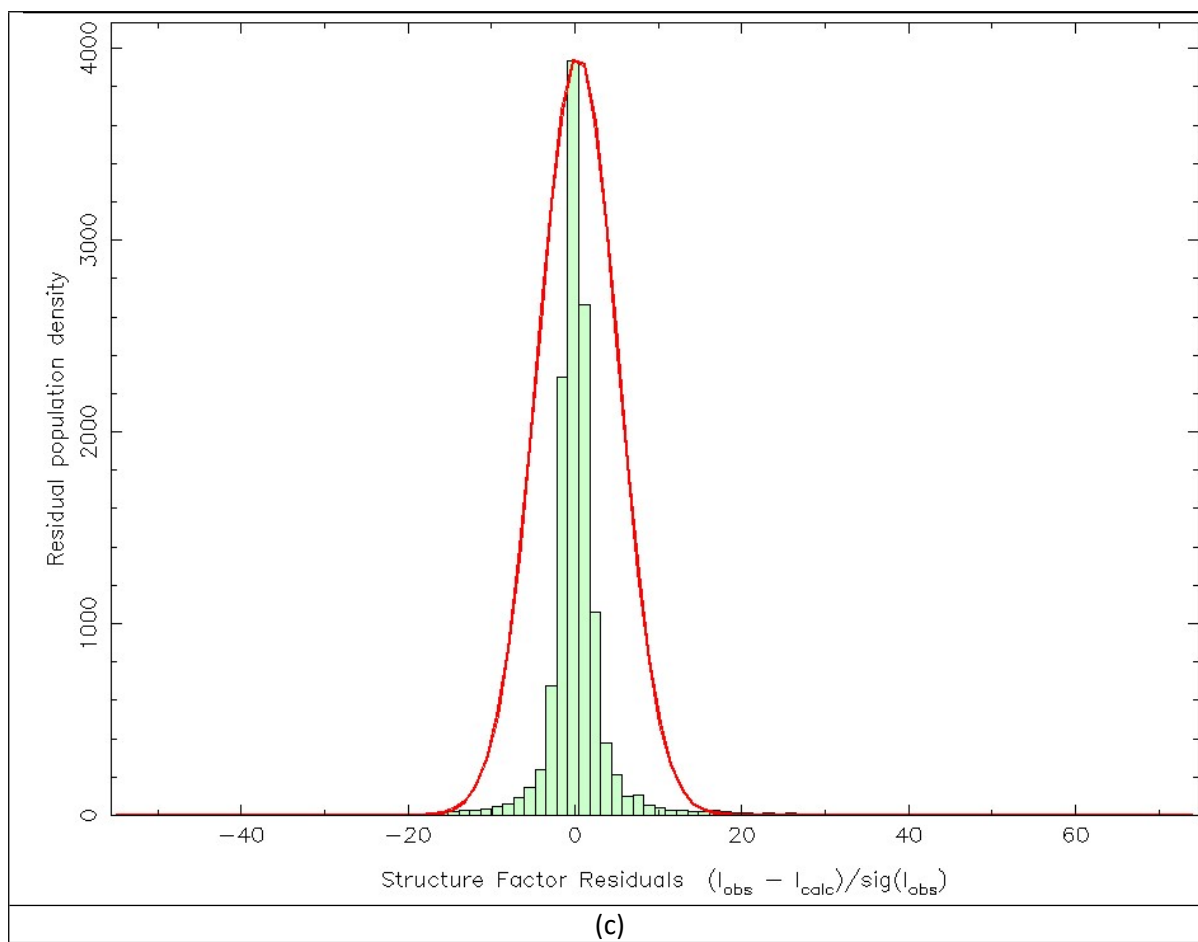
Figure S2. Residual density plots generated in WingX, residual density vs. fractal dimension a, b and c are (1), (2) and (3) respectively. [3, 4]

Table S.1

Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for (1). Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
O4	8243.1(10)	2922.6(11)	5282.3(6)	17.38(17)
O1	4370.7(11)	1894.6(11)	8104.7(6)	17.63(18)
O2	7696.6(11)	3286.4(12)	8687.7(6)	20.81(19)
O5	4914.3(13)	3031.4(13)	1767.4(6)	24.4(2)
O3	9962.7(11)	3076.5(13)	6903.9(6)	23.3(2)
O1'	8435.6(13)	3963.8(13)	1091.4(7)	25.9(2)
C7	4546.2(15)	2406.1(14)	4934.3(8)	14.6(2)
C8	4515.4(15)	2338.8(14)	6056.1(8)	14.6(2)
C3	6242.4(15)	2636.9(14)	7949.1(8)	14.8(2)

C9	6662.7(16)	2958.6(15)	3524.0(8)	17.1(2)
C4	6289.6(15)	2591.4(14)	6764.5(8)	14.6(2)
C11	2925.9(16)	2383.4(16)	3113.7(9)	19.3(2)
C6	6458.8(14)	2751.0(14)	4579.4(8)	14.8(2)
C5	8276.3(15)	2882.9(15)	6382.0(8)	16.1(2)
C12	2762.5(15)	2211.6(15)	4170.9(8)	17.4(2)
C10	4875.9(16)	2787.1(15)	2793.7(8)	17.8(2)
C2	4080.4(16)	1981.9(16)	9245.3(8)	17.7(2)
C1	1899.0(17)	1024.2(18)	9227.8(9)	23.0(2)

Table S.2: Anisotropic Displacement Parameters (Å2×103) for (1) The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+...].

Atom	U11	U22	U33	U23	U13	U12
O4	11.3(3)	27.6(4)	13.9(3)	6.3(3)	2.6(3)	3.6(3)
O1	14.2(3)	24.8(4)	13.3(3)	5.7(3)	3.4(3)	-0.7(3)
O2	14.9(4)	31.0(4)	15.1(3)	6.3(3)	0.7(3)	0.4(3)
O5	22.5(4)	39.4(5)	13.1(4)	9.5(3)	3.6(3)	6.4(3)
O3	12.0(3)	39.8(5)	18.0(4)	8.0(3)	1.7(3)	3.7(3)
O1'	26.2(4)	29.1(4)	18.1(4)	4.4(3)	2.9(3)	-5.0(3)
C7	13.3(5)	16.5(5)	13.7(4)	3.0(3)	2.6(3)	3.3(3)
C8	12.1(4)	16.7(4)	15.3(4)	3.7(3)	4.0(3)	2.6(3)
C3	13.3(4)	16.9(4)	15.2(4)	5.0(3)	3.4(3)	3.6(4)
C9	15.4(5)	21.3(5)	15.0(4)	4.2(4)	4.5(4)	3.7(4)
C4	13.0(4)	17.3(4)	13.4(4)	3.8(3)	2.9(3)	2.2(4)
C11	16.1(5)	25.1(5)	16.0(5)	4.0(4)	0.3(4)	4.8(4)
C6	12.5(4)	17.2(4)	14.3(4)	2.9(3)	1.9(3)	3.2(4)
C5	14.6(4)	20.4(5)	13.6(4)	4.3(3)	3.3(3)	2.8(4)
C12	13.0(5)	22.0(5)	17.0(5)	4.0(4)	2.7(4)	3.6(4)
C10	20.6(5)	20.4(5)	12.6(4)	3.4(3)	3.2(4)	5.5(4)
C2	17.8(5)	22.6(5)	13.1(4)	6.1(4)	4.4(3)	0.9(4)
C1	18.5(5)	28.1(6)	23.2(5)	9.4(4)	6.2(4)	0.5(4)

Table S.3 Bond Lengths for (1).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O4	C6	1.3725(12)	C7	C12	1.4107(13)
O4	C5	1.3872(11)	C8	C4	1.3608(13)
O1	C3	1.3290(12)	C3	C4	1.4857(13)
O1	C2	1.4555(11)	C9	C6	1.3874(13)
O2	C3	1.2162(12)	C9	C10	1.3923(14)
O5	C10	1.3440(12)	C4	C5	1.4560(13)
O3	C5	1.2082(12)	C11	C12	1.3771(14)
C7	C8	1.4245(13)	C11	C10	1.4067(15)
C7	C6	1.3983(13)	C2	C1	1.5008(14)

Table S.4 Bond Angles for (1)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	O4	C5	122.99(8)	C12	C11	C10	120.15(9)
C3	O1	C2	116.24(8)	O4	C6	C7	120.53(8)
C6	C7	C8	118.06(9)	O4	C6	C9	116.81(8)
C6	C7	C12	118.08(9)	C9	C6	C7	122.65(9)
C12	C7	C8	123.83(9)	O4	C5	C4	116.53(8)
C4	C8	C7	121.26(9)	O3	C5	O4	115.58(9)
O1	C3	C4	110.77(8)	O3	C5	C4	127.88(9)
O2	C3	O1	123.92(9)	C11	C12	C7	120.30(9)
O2	C3	C4	125.30(9)	O5	C10	C9	122.42(10)
C6	C9	C10	117.97(9)	O5	C10	C11	116.74(9)
C8	C4	C3	120.77(9)	C9	C10	C11	120.82(9)
C8	C4	C5	120.51(9)	O1	C2	C1	107.39(8)
C5	C4	C3	118.69(8)				

Table S.5 Torsion Angles for (1)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C3	C4	C8	16.72(13)		C6	C7	C8	C4	-0.34(15)
O1	C3	C4	C5	-165.14(9)		C6	C7	C12	C11	-0.76(15)
O2	C3	C4	C8	-162.26(10)		C6	C9	C10	O5	177.67(9)
O2	C3	C4	C5	15.88(15)		C6	C9	C10	C11	-1.03(16)

C7	C8	C4	C3	176.33(8)	C5	O4	C6	C7	-3.82(15)
C7	C8	C4	C5	-1.77(15)	C5	O4	C6	C9	175.45(9)
C8	C7	C6	O4	3.09(14)	C12	C7	C8	C4	-178.11(9)
C8	C7	C6	C9	-176.14(9)	C12	C7	C6	O4	-179.01(8)
C8	C7	C12	C11	177.01(9)	C12	C7	C6	C9	1.76(15)
C8	C4	C5	O4	1.16(14)	C12	C11	C10	O5	-176.77(9)
C8	C4	C5	O3	-178.03(10)	C12	C11	C10	C9	1.99(16)
C3	O1	C2	C1	-178.46(9)	C10	C9	C6	O4	179.88(9)
C3	C4	C5	O4	-176.98(8)	C10	C9	C6	C7	-0.87(16)
C3	C4	C5	O3	3.83(16)	C10	C11	C12	C7	-1.06(16)
C6	O4	C5	O3	-179.07(9)	C2	O1	C3	O2	3.21(14)
C6	O4	C5	C4	1.64(14)	C2	O1	C3	C4	-175.79(8)

Table S.6 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for (1).

Atom	x	y	z	U(eq)
H1A	920(30)	1630(30)	8841(14)	39(4)
H1B	1610(20)	1180(20)	10009(13)	34(4)
H1C	1670(20)	-400(20)	8861(12)	24(3)
H1'A	8300(30)	3810(30)	400(17)	47(5)
H1'B	9320(30)	4940(30)	1409(16)	46(5)
H2A	5080(20)	1280(20)	9558(11)	22(3)
H2B	4340(20)	3380(20)	9644(11)	19(3)
H12	1420(20)	1980(20)	4408(12)	22(3)
H9	8010(20)	3220(20)	3313(13)	32(4)
H11	1750(20)	2270(20)	2603(12)	26(3)
H8	3230(20)	2150(20)	6333(11)	20(3)
H5	6150(40)	3400(30)	1657(18)	64(6)

Table S.7 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for (2) . Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
C2'	5148.1(12)	3639.0(11)	5129.7(8)	22.66(14)

C1'	5334.0(14)	3513.3(12)	6531.8(8)	25.53(15)
C3'	7918.6(11)	5167.9(9)	5860.2(7)	18.85(11)
C4'	9852.1(16)	6299.3(13)	5815.6(11)	30.73(18)
N1'	6802.0(10)	4692.8(8)	4719.6(6)	18.84(11)
N2'	7072.8(12)	4481.4(10)	6985.3(6)	22.91(13)

Table S.8 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for (2). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
C2'	24.5(2)	23.9(3)	19.5(2)	-1.2(2)	-0.92(19)	-5.1(2)
C1'	28.4(3)	30.0(4)	18.2(2)	0.0(2)	4.2(2)	-7.2(3)
C3'	23.0(2)	17.5(3)	16.04(19)	-1.36(18)	-0.33(17)	-1.11(19)
C4'	31.1(3)	30.3(4)	30.9(4)	0.0(3)	-1.6(3)	-12.1(3)
N1'	23.7(2)	18.3(2)	14.50(18)	0.46(16)	-0.41(14)	-0.16(18)
N2'	28.6(2)	25.6(3)	14.63(19)	-2.05(18)	1.42(18)	-3.6(2)

Table S.9 Bond Lengths for (2)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C2'	C1'	1.3666(11)	C3'	C4'	1.4852(11)
C2'	N1'	1.3732(10)	C3'	N1'	1.3499(9)
C1'	N2'	1.3822(10)	C3'	N2'	1.3266(9)

Table S.10 Bond Angles for (2).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1'	C2'	N1'	105.97(7)	N2'	C3'	N1'	111.13(6)
C2'	C1'	N2'	109.58(7)	C3'	N1'	C2'	107.66(6)
N1'	C3'	C4'	122.97(7)	C3'	N2'	C1'	105.66(6)
N2'	C3'	C4'	125.89(7)				

Table S.11 Torsion Angles for (2).

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2'	C1'	N2'	C3'	-0.35(10)	N1'	C2'	C1'	N2'	0.26(10)
C1'	C2'	N1'	C3'	-0.08(9)	N1'	C3'	N2'	C1'	0.30(9)
C4'	C3'	N1'	C2'	179.19(8)	N2'	C3'	N1'	C2'	-0.14(9)
C4'	C3'	N2'	C1'	-179.01(9)					

Table S.12 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for (2).

Atom	x	y	z	U(eq)
H4'B	10210(60)	7110(40)	6630(30)	115(11)
H4'C	9480(40)	7160(30)	5030(30)	78(8)
H4'A	11300(50)	5750(60)	6200(50)	161(17)
H2'	4130(30)	3150(20)	4357(17)	40(5)
H1'	4530(30)	2720(20)	7229(16)	38(4)
H1'A	7150(40)	5020(30)	3777(16)	65(6)

Table S.13 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for (3). Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
C1	7627.3(7)	8009.4(6)	12883.5(5)	26.17(8)
C1'	2270.5(6)	9157.7(4)	2010.7(4)	21.67(6)
C2'	1364.0(6)	10333.1(5)	1186.0(3)	20.73(6)
C2	8098.0(6)	6488.2(5)	12755.1(4)	21.61(6)
C3'	1316.3(5)	10802.4(4)	3018.8(3)	16.01(5)
C3	7954.3(5)	5334.0(4)	11180.6(3)	15.24(5)
C4	7203.9(4)	5485.9(4)	9971.7(3)	14.25(5)
C4'	983.9(6)	11638.3(4)	3978.6(4)	20.42(6)
C5	7699.2(5)	4283.2(4)	9391.8(3)	15.07(5)
C6	5963.2(4)	5753.4(3)	7635.8(3)	14.08(5)

C7	5469.6(4)	6912.1(4)	8188.1(3)	14.70(5)
C8	6123.6(4)	6739.3(4)	9374.2(3)	15.00(5)
C9	5410.9(5)	5816.0(4)	6478.4(3)	16.29(5)
C10	4316.8(5)	7092.3(4)	5832.7(3)	16.60(5)
C11	3819.1(5)	8286.7(4)	6361.0(3)	18.81(6)
C12	4379.5(5)	8186.1(4)	7518.8(3)	18.09(6)
N1'	763.4(4)	11359.3(3)	1842.1(3)	17.52(5)
N2'	2232.0(5)	9458.3(4)	3159.0(3)	18.93(5)
O1	7359.2(4)	6507.5(3)	11603.3(3)	19.22(5)
O2	9009.4(4)	4288.7(3)	11729.0(3)	20.21(5)
O3	8630.4(5)	3109.7(3)	9802.9(3)	21.10(5)
O4	7025.6(4)	4490.3(3)	8241.3(2)	16.11(4)
O5	3766.6(5)	7122.5(3)	4733.2(3)	22.08(6)

Table S.14 Anisotropic Displacement Parameters (Å2×103) for (3). The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+...].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	32.92(19)	23.89(18)	25.61(16)	-13.04(14)	-4.32(14)	-3.56(14)
C1'	29.97(16)	16.26(14)	18.51(12)	-5.28(10)	-8.39(11)	1.25(11)
C2'	28.17(15)	18.78(14)	15.37(11)	-3.49(10)	-8.43(10)	-1.87(11)
C2	27.36(15)	20.99(15)	18.18(12)	-8.19(11)	-8.46(11)	0.10(12)
C3'	19.59(11)	13.39(11)	14.2(1)	-1.72(8)	-6.22(8)	-0.89(8)
C3	17.68(10)	13.37(11)	14.43(10)	-3.53(8)	-5.05(8)	-0.26(8)
C4	16.53(10)	12.21(11)	13.55(9)	-3.00(8)	-4.67(8)	-0.12(8)
C4'	27.06(15)	17.02(14)	17.34(12)	-5.04(10)	-4.95(10)	-1.77(11)
C5	18.16(10)	12.25(11)	13.65(9)	-2.47(8)	-5.48(8)	0.98(8)
C6	16.6(1)	10.96(10)	13.46(9)	-2.00(7)	-4.85(7)	0.64(8)
C7	17.67(10)	11.26(11)	14.3(1)	-2.69(8)	-5.42(8)	0.82(8)
C8	17.71(10)	12.11(11)	14.8(1)	-3.45(8)	-4.94(8)	0.18(8)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C9	20.59(12)	13.17(11)	14.21(10)	-3.00(8)	-6.47(8)	1.10(9)
C10	20.48(12)	13.87(12)	14.3(1)	-2.24(8)	-6.53(8)	0.48(9)
C11	23.98(13)	13.06(12)	17.63(11)	-2.62(9)	-8.67(10)	2.76(10)
C12	23.24(13)	12.26(12)	17.70(11)	-3.85(9)	-7.92(10)	2.76(9)
N1'	21.53(11)	14.19(11)	15.36(9)	-0.78(8)	-7.92(8)	-0.44(8)
N2'	25.38(12)	14.05(11)	15.89(10)	-2.18(8)	-8.75(9)	1.50(9)
O1	23.82(11)	16.85(11)	17.81(10)	-7.43(8)	-8.77(8)	2.79(8)
O2	25.40(11)	15.43(11)	18.69(10)	-3.88(8)	-10.67(8)	3.27(8)
O3	28.67(12)	13.69(10)	18.82(10)	-3.98(8)	-11.13(9)	5.97(9)
O4	20.89(10)	11.84(9)	14.49(8)	-3.28(6)	-7.55(7)	2.88(7)
O5	31.69(14)	16.93(11)	16.54(9)	-3.85(8)	-12.44(9)	3.59(9)

Table S.15 Bond Lengths for (3).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.5028(6)	C4	C8	1.3650(4)
C1'	C2'	1.3640(5)	C5	O3	1.2103(4)
C1'	N2'	1.3850(5)	C5	O4	1.3833(4)
C2'	N1'	1.3742(5)	C6	C7	1.4025(5)
C2	O1	1.4562(4)	C6	C9	1.3849(4)
C3'	C4'	1.4886(5)	C6	O4	1.3675(4)
C3'	N1'	1.3492(4)	C7	C8	1.4207(4)
C3'	N2'	1.3272(5)	C7	C12	1.4074(4)
C3	C4	1.4828(4)	C9	C10	1.4011(5)
C3	O1	1.3346(4)	C10	C11	1.4169(5)
C3	O2	1.2151(4)	C10	O5	1.3323(4)
C4	C5	1.4601(5)	C11	C12	1.3777(5)

Table S.16 Bond Angles for(3).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2'	C1'	N2'	109.42(3)	O4	C6	C7	120.29(3)
C1'	C2'	N1'	105.75(3)	O4	C6	C9	116.98(3)
O1	C2	C1	106.85(3)	C6	C7	C8	118.21(3)
N1'	C3'	C4'	123.23(3)	C6	C7	C12	117.73(3)
N2'	C3'	C4'	126.34(3)	C12	C7	C8	124.05(3)
N2'	C3'	N1'	110.39(3)	C4	C8	C7	121.55(3)
O1	C3	C4	111.93(3)	C6	C9	C10	118.54(3)
O2	C3	C4	125.19(3)	C9	C10	C11	119.90(3)
O2	C3	O1	122.87(3)	O5	C10	C9	117.71(3)
C5	C4	C3	118.81(3)	O5	C10	C11	122.39(3)
C8	C4	C3	121.38(3)	C12	C11	C10	120.15(3)
C8	C4	C5	119.77(3)	C11	C12	C7	120.95(3)
O3	C5	C4	127.59(3)	C3'	N1'	C2'	108.30(3)
O3	C5	O4	115.47(3)	C3'	N2'	C1'	106.14(3)
O4	C5	C4	116.93(3)	C3	O1	C2	115.88(3)
C9	C6	C7	122.74(3)	C6	O4	C5	123.24(3)

Table S.17 Torsion Angles for (3).

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	O1	C3	166.50(4)	C9	C6	C7	C8	-179.44(3)
C1'	C2'	N1'	C3'	0.44(5)	C9	C6	C7	C12	-0.52(5)
C2'	C1'	N2'	C3'	-0.21(5)	C9	C6	O4	C5	178.93(3)
C3	C4	C5	O3	2.83(6)	C9	C10	C11	C12	-1.24(6)
C3	C4	C5	O4	-177.62(3)	C10	C11	C12	C7	0.85(6)
C3	C4	C8	C7	177.12(3)	C12	C7	C8	C4	-178.86(3)
C4	C3	O1	C2	-176.99(3)	N1'	C3'	N2'	C1'	0.49(5)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C4	C5	O4	C6	0.94(5)	N2'	C1'	C2'	N1'	-0.14(5)
C4'	C3'	N1'	C2'	177.05(4)	N2'	C3'	N1'	C2'	-0.60(5)
C4'	C3'	N2'	C1'	-177.06(4)	O1	C3	C4	C5	-178.99(3)
C5	C4	C8	C7	-0.39(5)	O1	C3	C4	C8	3.48(5)
C6	C7	C8	C4	-0.02(5)	O2	C3	C4	C5	2.15(6)
C6	C7	C12	C11	0.02(6)	O2	C3	C4	C8	-175.38(4)
C6	C9	C10	C11	0.74(6)	O2	C3	O1	C2	1.90(6)
C6	C9	C10	O5	-178.62(3)	O3	C5	O4	C6	-179.46(3)
C7	C6	C9	C10	0.14(6)	O4	C6	C7	C8	0.88(5)
C7	C6	O4	C5	-1.37(5)	O4	C6	C7	C12	179.79(3)
C8	C4	C5	O3	-179.60(4)	O4	C6	C9	C10	179.83(3)
C8	C4	C5	O4	-0.05(5)	O5	C10	C11	C12	178.09(4)
C8	C7	C12	C11	178.87(4)					

Table S.18 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for(3).

Atom	x	y	z	U(eq)
H1A	8237(15)	8705(11)	12172(10)	41(3)
H1B	8092(14)	8029(12)	13668(9)	38(2)
H1C	6279(13)	8366(12)	12949(10)	40(3)
H2A	9449(12)	6118(10)	12693(9)	30(2)
H2B	7547(12)	5787(10)	13455(8)	27(2)
H5	3205(18)	8103(12)	4263(12)	59(3)
H8	5774(13)	7593(11)	9737(9)	29(2)
H9	5848(12)	4927(9)	6159(8)	26(2)
H11	3063(12)	9175(10)	5874(9)	28(2)
H12	4033(14)	9042(11)	7895(10)	36(2)

H1'	2917(13)	8192(10)	1905(10)	36(2)
H2'	1118(15)	10561(12)	288(9)	41(3)
H1'A	45(14)	12253(10)	1558(10)	38(3)
H4'A	470(13)	11128(10)	4781(8)	30(2)
H4'B	119(14)	12567(11)	3707(10)	39(3)
H4'C	2128(14)	11878(12)	4130(10)	40(3)

Optimised Cartesian coordinates of (1)

1.a

atom	X	y	Z
O	4.35518799686038	0.68074139856511	6.40956147961230
O	1.61825080984055	-1.20063843007194	9.79773588871354
O	3.73560588681723	-0.80995686121660	10.38758832685085
O	2.61313942729582	1.55082725354477	2.09226185365889
O	5.31746772647657	0.33616084331304	8.34939038627477
C	2.06171107611146	0.17811766413193	5.95587663650362
C	1.94376390365480	-0.28886577875222	7.29715833996193
C	2.85956831276412	-0.77521058534919	9.55625062332631
C	3.53926051894917	1.12994612246327	4.25448095046401
C	3.00139479777498	-0.27172844289806	8.16117987939856
C	1.20360991258223	0.64129578072710	3.73535254342598
C	3.31480359238787	0.66054657444936	5.54362384257820
C	4.30010107006975	0.24587380258452	7.71405833309338
C	1.00584568875271	0.18057999508517	5.01672705350783
C	2.47828757922852	1.12054159375979	3.33984435969722
C	1.34492832054697	-1.71337820047932	11.10807808949898
C	-0.10728305780649	-2.12359315620519	11.15100218262856
H	-0.76357859475659	-1.26357671753685	10.95336352467854
H	-0.35004961846888	-2.52211030045607	12.14636688308125
H	-0.31754831238703	-2.90419263145693	10.40536391561466
H	2.01782372927858	-2.56262708347773	11.30384375164637

H	1.57239253293675	-0.93178486614169	11.84952469298097
H	0.02511227516126	-0.19016445376686	5.32653818155505
H	4.52499230433266	1.49477271230238	3.96146545428050
H	0.39485191868440	0.64729225693402	3.00217522735308
H	0.98017069906348	-0.67185004303671	7.64137331950539
H	3.54155041899086	1.85653432243216	1.91759385229770
O	5.13131192752868	2.29202235990326	1.70361332783885
H	5.55801944085961	1.76278106104780	1.01618734236756
H	5.23667471646939	3.20507580960169	1.40437675760453

1.b

atom	X	y	Z
O	4.35157971326302	0.77664382715093	6.45055833442822
O	1.60972081818931	-1.06495840332273	9.84860322104277
O	3.72635264807711	-0.68606767857385	10.43820485854189
O	2.68734138006330	1.35770375982767	2.04930393308888
O	5.26823150051984	0.60752625695909	8.42584837684016
C	2.10176652783707	0.13761848575633	5.95758973326543
C	1.97113152972786	-0.27971980048820	7.31416584551047
C	2.84921607148433	-0.65137144367861	9.60580076416049
C	3.57883467016695	1.08420035175122	4.25438494096524
C	3.00247889710028	-0.17097585871085	8.20313616142723
C	1.28599727258283	0.45346728809701	3.69724246027630
C	3.34015867049742	0.66289576706217	5.55873541927525
C	4.27589953378044	0.40940703469920	7.76746783718303
C	1.07386069526744	0.04197251014014	4.99309548459926
C	2.54546734067515	0.97740803943299	3.32182931734623
C	1.33185903549892	-1.58594105733375	11.15750619569772
C	-0.10786682277312	-2.03845807256977	11.17848619867984
H	-0.78726221757853	-1.19869077390733	10.97226272905275
H	-0.35191190774997	-2.44495470627966	12.17024958711069

H	-0.28290601449536	-2.82467725979631	10.42958216104999
H	2.02735445294021	-2.41437981662310	11.36169666650400
H	1.52656920866873	-0.79584048396867	11.89915980625060
H	0.10517177994782	-0.36498959340633	5.29403854120297
H	4.55581672902451	1.48668262648300	3.97756047322672
H	0.50210706464088	0.38333990214471	2.94091729222323
H	1.02150999615797	-0.70349865569591	7.64887688261218
H	3.57591025637427	1.70467990922052	1.89012810065377
O	5.88386293456958	1.02290704311494	11.18469598828404
H	5.20208030091285	0.42739696147211	11.51761029560539
H	5.74715993462864	0.91572984104306	10.23009639389450

1.c

atom	X	y	Z
O	4.49123439048453	0.99383033897605	5.77332328389629
O	1.64358564707545	-0.58862935147024	9.21559794428205
O	3.78463159498243	-0.32883889366807	9.79620254838314
O	2.88636832832899	1.51943829947616	1.34444078266424
O	5.36741161323233	0.86255867231912	7.77923691741786
C	2.24672956342000	0.34573698686075	5.26132240021587
C	2.08776646230907	-0.02801753808242	6.63182694171357
C	2.91523238716386	-0.28336984609277	8.95894778730107
C	3.74879470133136	1.25803309824580	3.56264248751371
C	3.10124274588029	0.10786310412924	7.53244866266772
C	1.45498846734643	0.65524174943347	2.99036216422572
C	3.49286339260047	0.85963667586219	4.87078547912217
C	4.39354601949406	0.65886923487611	7.10488710543654
C	1.22804858504941	0.25492945448873	4.28997452183516
C	2.72438686884076	1.15139697010255	2.62177609311668
C	1.32627376520822	-1.02719660718729	10.54334221651070
C	-0.16412179720170	-1.25913595835558	10.60615354132938
H	-0.71399751378966	-0.32988286561972	10.39517749665049

H	-0.44399311127807	-1.60440530091030	11.61149607907420
H	-0.47440013823384	-2.02299321890382	9.87831340882378
H	1.89543015855731	-1.94528041187891	10.75745580182823
H	1.65304841553346	-0.25427469964362	11.25458118314527
H	0.24853838854145	-0.12857703997273	4.58692318098112
H	4.72850011554080	1.65826242264459	3.29284969161954
H	0.67167679289728	0.60043653887255	2.23253250364555
H	1.12603736353293	-0.42546436074361	6.96431272354612
H	3.79194626951211	1.81875090756911	1.18537206311521
O	-0.28204716757750	2.83396030043813	6.30817835217143
O	2.56551916182505	4.41645493417663	2.86584924721938
O	0.42448435666198	4.15654077370280	2.28525933930319
O	1.32292157412980	2.30836837231044	10.73702506621908
O	-1.15824520630523	2.96515756121840	4.30226925740277
C	1.96246447011210	3.48207105687752	6.82013004735114
C	2.12139756661578	3.85581798255623	5.44962061389202
C	1.29388997160498	4.11113193484770	3.12251085592039
C	0.46043923955999	2.56977576546950	8.51884544395324
C	1.10790885717956	3.71991171134337	4.54901695633963
C	2.75425966036607	3.17256750374718	9.09107010078717
C	0.71634083556906	2.96816749170776	7.21069557056237
C	-0.18437772631612	3.16888642883746	4.97660465851615
C	2.98116846488250	3.57288257812226	7.79145312687393
C	1.48486999483280	2.67641342668166	9.45968658294409
C	2.88280297124186	4.85500505703906	1.53809256301815
C	4.37318296531273	5.08704073537038	1.47527542591092
H	4.92311876949699	4.15783150575585	1.68628760404762
H	4.65303317001977	5.43229068747090	0.46992033735747
H	4.68340969099074	5.85094561894698	2.20308772069263
H	2.31358622003242	5.77304492125763	1.32395115893126
H	2.55608099547003	4.08204038495334	0.82687600986444

H 3.96067082723044   3.95639083074891   7.49448089166003

H -0.51925693355761   2.16954040190716   8.78866253345994

H 3.53758948263793   3.22736997536942   9.84888124152305

H 3.08311462444070   4.25327702010783   5.11711488291574

H 0.41734268718302   2.00907367770781   10.89612040110020

Optimised Cartesian coordinates of (2)

2.

atom	X	y	Z
C	3.16815035624237	2.90169646431372	4.96573897085681
C	3.17003148805310	2.94437220749536	6.33496802119502
C	4.75940171303602	4.24178032058318	5.71792358401945
C	5.91268725021165	5.18950570627317	5.70308777966245
N	4.19179083733755	3.73712061280932	4.58353260703127
N	4.15946450478901	3.77783678012166	6.78717375007567
H	6.15436918698149	5.45083582883504	6.73995244846457
H	5.67490733028564	6.11466505391724	5.15517806451751
H	6.80495468667300	4.73901657775712	5.24057128545958
H	2.55027094650257	2.36729035737294	4.24858256074211
H	2.50807060570228	2.41533561284928	7.01953575925712
H	4.47088409418529	3.94303147767194	3.63426216871841

2.a.

atom	X	y	Z
C	3.44329208044931	2.62413258725491	4.94417933591898
C	3.56017855124174	2.53433489431498	6.30555922651943
C	4.63675259415717	4.31550861448862	5.72434942736761
C	5.47339571887272	5.55012615331393	5.73936404813692
N	4.13243020383143	3.76011186962476	4.59682211126085
N	4.30398518246589	3.59089823820696	6.77652018548568
H	5.46516509838350	5.98703286743700	6.74601110440423

H	5.09558011312484	6.29493761372100	5.02515540793120
H	6.51647765847138	5.32113591375458	5.47175483747061
H	2.94004374430854	2.00111077319468	4.20889771188832
H	3.14968813231823	1.77680730067057	6.97238339865289
H	4.24456591362802	4.12608264898394	3.65714914758543
C	6.20599326816064	4.76506536268334	9.90211541454981
C	6.06564430346149	4.89059355743832	11.26253759575984
C	4.23749968139608	4.02587207479039	10.54363993102878
C	2.86708798871974	3.43786116004476	10.44536254078320
N	5.03193702343947	4.21257254373321	9.46131647238802
N	4.83282038516410	4.42567634456708	11.65365205170629
H	2.42234626840764	3.38651416150456	11.44701361612436
H	2.89550963761004	2.42203796204209	10.02200427066268
H	2.21466201475907	4.04808261040311	9.80214270103473
H	7.01951764542894	5.01558703421715	9.22400800724344
H	6.78668419356195	5.28895210970430	11.97752622253753
H	4.78274259863797	3.97856560390560	8.47415123355891

Optimised Cartesian coordinates of (3)

3.a.

atom	X	y	Z
C	9.92882592658703	11.68862238812035	13.06416213569308
C	9.65253926521807	10.20747726756436	13.15804170694177
C	8.57970268774137	8.53490506831273	11.88154775419459
C	7.79755153908871	8.27705083245152	10.64052887841786
C	7.32669096799723	6.91661315258674	10.35541365428580
C	6.35352686914929	7.75150130838971	8.30270052873554
C	6.78843630584244	9.06303113171182	8.56388688478444
C	7.51843696319461	9.28883098875457	9.76489734427827
C	5.64652891691889	7.42524316253044	7.15403414146723
C	5.35806046674321	8.43018536582641	6.21813695751295
C	5.78407027231553	9.76406184226431	6.46737257859129

C	6.48291126887530	10.06372209453466	7.61517128657033
O	8.88376858782487	9.82807475049671	12.00886602853143
O	8.91863891938402	7.70340185066582	12.69031674244037
O	7.47790945327614	5.92594206956104	11.02145025610923
O	6.62478909372312	6.75803186111601	9.18224387818952
O	4.69056352644604	8.09670667621598	5.12880585395711
H	10.50444323939618	11.92406231803397	12.15702081572534
H	10.51414780113373	12.01034771473640	13.93735118805728
H	8.99148576022824	12.26349940567634	13.04517737599886
H	10.58165150988004	9.61708373626207	13.17424413773868
H	9.08151952611321	9.95313484579728	14.06464153970071
H	4.60357887685915	8.86918100572985	4.46718138903003
H	7.86800127499190	10.29944316914448	9.98854489716863
H	5.32735718663935	6.39766047275743	6.97402916982252
H	5.55394011634982	10.54170873110264	5.73706548772038
H	6.81098017211789	11.08888191273484	7.80644821580930
C	5.24780372034225	10.34722722290077	2.30869826791832
C	4.77216193955430	11.46210113379438	1.67498523280452
C	3.48307882884363	10.96799994854676	3.40491598367845
C	2.37862264126931	11.05083683558105	4.40173042202506
N	3.65677474752759	11.83724818432558	2.38427653220770
N	4.43597172567402	10.05223638954015	3.38020776833378
H	6.11858129731014	9.74198648973256	2.06176746883436
H	5.11788600913412	12.01118371812522	0.80271347379743
H	3.06106431846451	12.63300034316200	2.17958764041233
H	2.49253051048354	10.23964266146180	5.13130383944275
H	1.39721293872679	10.95402553628015	3.91455048148653
H	2.40013382863434	12.01260741347083	4.93465006158603

3.b

atom	X	y	Z
O	8.68088864978792	9.60325221060707	12.24958044144739

O	9.24716453396237	7.45723259608543	12.53973619477711
O	8.43786977878665	5.79423800489137	10.42268971507283
O	7.38330713158354	6.70984214633266	8.73369920212791
O	5.03184524081408	8.26024731980923	5.01318964732329
C	9.10038082709629	11.41412550373006	13.73080970141170
C	9.25923344627404	9.92745066667328	13.51654343065035
C	8.72824237867760	8.32615531938594	11.85096376930891
C	8.09772311401174	8.15958824077987	10.54233601437016
C	8.01867633494403	6.83325757833158	9.96680842355756
C	6.83051986348444	7.75066157003260	8.07289497245081
C	6.91729392795093	9.09372156566581	8.61567231648485
C	7.56144328267355	9.28712977609016	9.84269495631494
C	6.20043592192074	7.48962718131718	6.88183009059096
C	5.62487530697244	8.55514867474497	6.15656463215442
C	5.69224652961428	9.89264794296695	6.65352182242348
C	6.31774734423244	10.14992862851039	7.84412707236754
H	9.61262106576510	11.98135261276528	12.93982730180270
H	9.53764485091530	11.69811280743686	14.69862999692860
H	8.03804376203597	11.69930418374873	13.73452969516138
H	10.31828142609345	9.62424397932640	13.51403212729587
H	8.75023972072052	9.34454230115906	14.30086474025081
H	4.67215145554054	9.05169528518971	4.58270830405234
H	7.64323262014547	10.28381815655407	10.27196767657513
H	6.14588832064123	6.47162789334240	6.49349894223483
H	5.23718774698637	10.69796699290648	6.07022621934220
H	6.37186705202591	11.16938377352668	8.23238725561546
N	10.10338328710193	4.75999847116249	12.67895544053108
N	11.24377689846828	3.34886967098074	13.93840225139407
C	10.78096704340913	2.69265736518543	12.82288448237503
C	10.06875435934945	3.55538341634178	12.02666951914813
C	10.81768270347983	4.59430015433925	13.81957421761748

C	11.08645813346711	5.71231871000088	14.77554982825306
H	10.98133879402292	1.63446183564066	12.65071401392611
H	9.54897571842348	3.42870259239763	11.08028999236462
H	9.66563620397679	5.63669524298075	12.37030211614228
H	10.92174645731741	5.38048626027941	15.81010910225715
H	10.43195367248531	6.56717639289107	14.56218735665555
H	12.13027309484122	6.05418297588952	14.69633701724159

3.c

atom	X	y	Z
O	2.44832642657282	2.80260568639715	-1.39296735378576
O	1.10914098939816	4.55622612434007	-1.03243897054777
O	2.54557371528815	6.54734989577873	0.46543950059191
O	3.83522191556958	5.73720765313951	2.04823472031677
O	6.59288168344921	4.39842408160195	5.59415809430350
C	2.11855608049580	1.02469782078067	-2.94173684859510
C	1.56697360195345	2.32956653292459	-2.42067136186412
C	2.08572920430760	3.90626905535400	-0.74302442973278
C	3.00226589715310	4.19741280827256	0.39418579471422
C	3.06966484653258	5.56489671699120	0.92017207945593
C	4.52361656250874	4.74650106605915	2.66573534899518
C	4.51438292633451	3.44293183376187	2.14445730910783
C	3.72579309476038	3.20217563895567	0.97677840969600
C	5.22316892362289	5.07129532632184	3.82235186591530
C	5.92973281824149	4.06343381569413	4.48135663739644
C	5.93307723039022	2.74255666506794	3.98043728770800
C	5.23283776627683	2.44391493076806	2.83029981656161
H	2.18219252851539	0.27683630501604	-2.13760586919510
H	1.45721792897838	0.63286260458367	-3.72760078071007
H	3.12160718699763	1.16415274882694	-3.37047117329974
H	0.56011462989267	2.20930391119429	-1.99128675995994
H	1.50157636216412	3.09402822082397	-3.21023223894496

H 7.04126012567013   3.62689458526414   5.96612377417123

H 3.67752085436820   2.19017790082000   0.56665093716799

H 5.21572980047733   6.09110205972959   4.20909014276821

H 6.48815040038832   1.96775890593309   4.51577825118322

H 5.21545954571515   1.42231588427978   2.44418321306139

N 0.54884761895358   1.86626404271255   1.50230734751436

N 2.09530928587171   0.82599409892837   2.67700492113314

C 1.79568688314812   0.08094828979233   1.56013763074966

C 0.83218354941007   0.71194115117242   0.81609594071374

C 1.32945501972459   1.89708674208674   2.61575261181558

C 1.28916541786929   3.00942982767321   3.60920670197771

H 2.28816332433676   -0.86875787704786   1.35076719706916

H 0.33281635347295   0.45034789555049   -0.11374688924589

H -0.12253983139094   2.57459427381593   1.22526797563035

H 0.34258718153550   3.01097709581673   4.17123636698783

H 1.38523425530722   3.98814588333192   3.11489186827636

H 2.11724289573804   2.88799979748634   4.31897693089848

Topological Parameters

Table S.19: List of bond critical points (BCP's) found from topological analysis of theoretical model ground states of 1.a

Bond	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})	ε
C(4)-C(5)	1.85682	-16.435	0.165215
C(11)-C(12)	2.12917	-19.2932	0.266391
C(11)-C(10)	2.021203	-18.5279	0.204374
C(11)-H(11)	1.866848	-25.0545	0.021981
C(12)-H(12)	1.880777	-25.7418	0.005705
C(1)-C(2)	1.725436	-14.9468	0.036424
C(2)-H(2A)	1.892593	-25.7225	0.043144
C(2)-H(2B)	1.892681	-25.7288	0.043086
C(1)-H(1A)	1.82849	-23.459	0.006627
C(1)-H(1B)	1.825454	-23.4548	0.004796
C(1)-H(1C)	1.828247	-23.4555	0.00665
C(7)-C(6)	2.063083	-18.8722	0.235536
C(7)-C(12)	1.997024	-17.6288	0.179774
C(7)-C(8)	1.966926	-17.6196	0.1242
C(8)-C(4)	2.175052	-19.8026	0.278237

C(8)-H(8)	1.908782	-27.2464	0.008534
C(3)-C(4)	1.794911	-15.8067	0.141477
C(9)-C(6)	2.098006	-19.3395	0.279905
C(9)-C(10)	2.062854	-18.6446	0.254967
C(9)-H(9)	1.864331	-25.2338	0.026394
H(9)-O(1')	0.068617	0.854929	0.357906
H(5)-O(1')	0.329468	3.843443	0.047085
O(4)-C(6)	1.914829	-3.73006	0.048263
O(4)-C(5)	1.850315	-8.94448	0.047386
O(1)-C(2)	1.585192	-5.73833	0.023746
O(1)-C(3)	2.090198	-8.94839	0.007923
O(1)-H(8)	0.111847	1.955906	5.09087
O(1')-H(1'B)	2.339779	-60.1309	0.018791
O(1')-H(1'A)	2.341216	-60.1988	0.018778
O(2)-C(3)	2.7987	6.086028	0.093869
O(2)-O(3)	0.088471	1.04155	0.33246
O(5)-C(10)	2.113372	-7.40406	0.032795
O(5)-H(5)	2.138469	-54.4971	0.013778
O(3)-C(5)	2.839271	6.249924	0.120695

Table S.20: List of ring critical points (RCP's) found from topological analysis of the theoretical ground state of 1.a

Atoms	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})
O(1)-H(8)-C(8)C(4)-C(3)	0.016568	0.087026
O(2)-O(3)-C(3)-C(4)-(C5)	0.012567	0.059555
O(4)-C(6)-C(7)-C(8)-C(4)C5)	0.020533	0.156759
C(10)-C(11)-C(12)-C(7)-C(6)-C(9)	0.02006	0.16721
O(5)--H(5)-O(1')-H(9)-C(9)-C(1)	0.008434	0.0422

Table S.21: Atomic charges (e) from the theoretical ground state of 1.a

Name	Ω
C(4)	-0.02735
C(11)	0.003962
C(6)	0.526327
C(5)	1.593385
C(12)	0.021828
C(10)	0.647268
C(2)	0.537192
C(1)	0.141688
C(7)	0.00264
C(8)	0.028735

C(3)	1.685323
C(9)	-0.00411
H(1C)	-0.02394
H(1B)	-0.01606
H(1A)	-0.02387
H(2A)	0.003001
H(2B)	0.003288
H(12)	0.038525
H(9)	0.061309
H(11)	0.029052
H(8)	0.090709
H(5)	0.688649
H(1'B)	0.66604
H(1'A)	0.666194
O(4)	-1.15491
O(1)	-1.15669
O(1')	-1.27116
O(2)	-1.24925
O(5)	-1.26306
O(3)	-1.24432
-----	0.000405

Table S.22: List of bond critical points (BCP's) found from topological analysis of the theoretical first excited state of 1.a

Bond	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})	ε
C(4)-C(5)	1.914309	-17.1965	0.196022
C(11)-C(12)	2.160941	-19.8395	0.275228
C(11)-C(10)	1.97277	-17.8022	0.191316
C(11)-H(11)	1.86589	-25.0767	0.022612
C(12)-H(12)	1.886681	-25.9964	0.004149
C(1)-C(2)	1.721651	-14.8906	0.03743
C(2)-H(2A)	1.886904	-25.5011	0.04305
C(2)-H(2B)	1.887262	-25.5143	0.043077
C(1)-H(1A)	1.826635	-23.392	0.006207
C(1)-H(1B)	1.824934	-23.4286	0.004865
C(1)-H(1C)	1.826979	-23.4053	0.006225
C(7)-C(6)	1.902371	-16.318	0.209995
C(7)-C(12)	1.907939	-16.2587	0.167277
C(7)-C(8)	2.05977	-18.9852	0.15703
C(8)-C(4)	1.92624	-15.686	0.250417
C(8)-H(8)	1.928467	-28.0288	0.009311
C(3)-C(4)	1.865532	-16.7865	0.165166

C(9)-C(6)	2.164173	-20.5657	0.291826
C(9)-C(10)	2.001916	-17.6895	0.239895
C(9)-H(9)	1.863447	-25.2049	0.027546
H(9)-O(1')	0.068023	0.861773	0.392346
H(5)-O(1')	0.38807	4.150317	0.044609
O(4)-C(6)	1.941377	-5.05638	0.047087
O(4)-C(5)	1.763504	-10.2096	0.04643
O(1)-C(2)	1.616336	-5.79793	0.021018
O(1)-C(3)	2.030941	-10.3305	0.013194
O(1')-H(1'B)	2.333091	-60.5222	0.018397
O(1')-H(1'A)	2.334218	-60.5254	0.091803
O(2)-C(3)	2.746481	3.410774	0.493532
O(2)-O(3)	0.087216	1.033236	0.035267
O(5)-C(10)	2.184681	-5.49334	0.012579
O(5)-H(5)	2.048385	-49.7136	0.120392
O(3)-C(5)	2.809915	4.592578	0

Table S.23: List of ring critical points (RCP's) found from topological analysis of the theoretical excited state of 1.a

Atoms	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})
O(2)-O(3)-C(3)-C(4)-(C5)	0.012581	0.057528
O(4)-C(6)-C(7)-C(8)-C(4)C(5)	0.01942	0.14568
C(10)-C(11)-C(12)-C(7)-C(6)-C(9)	0.019077	0.157373
O(5)--H(5)-O(1')-H(9)-C(9)-C(1)	0.00856	0.043258

Table S.24: Atomic charges (e) from the theoretical excited state of 1.a

Name	Ω
C(4)	-0.03748
C(11)	0.004904
C(6)	0.540574
C(5)	1.535624
C(12)	0.020991
C(10)	0.685492
C(2)	0.552793
C(1)	0.141322
C(7)	-0.00646
C(8)	-0.67402
C(3)	1.640861
C(9)	-0.00067
H(1C)	-0.0257

H(1B)	-0.01805
H(1A)	-0.02555
H(2A)	-0.00242
H(2B)	-0.00234
H(12)	0.044286
H(9)	0.062191
H(11)	0.033353
H(8)	0.104482
H(5)	0.690926
H(1'B)	0.670116
H(1'A)	0.670288
O(4)	-1.1314
O(1)	-1.15194
O(1')	-1.26945
O(2)	-1.24334
O(5)	-1.26977
O(3)	-1.24401
-----	-0.70439

Table S.25: List of bond critical points (BCP's) found from topological analysis of the theoretical ground state of 3.a

Bond	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})	ε
C(1)-C(2)	1.72549	-14.94633339	0.036137
C(1)-H(1A)	1.827991	-23.44334914	0.006709
C(1)-H(1B)	1.825359	-23.44949433	0.004728
C(1)-H(1C)	1.828382	-23.4559528	0.006661
C(10)-C(11)	1.998393	-18.01960362	0.200359
C(10)-O(5)	2.148429	-7.557476303	0.030613
C(11)-C(12)	2.124965	-19.21374676	0.264565
C(11)-H(11)	1.871322	-25.21145311	0.022932
C(12)-C(12)	1.88077	-25.7147322	0.005538
C(2)-H(2A)	1.893578	-25.75878478	0.042684
C(2)-H(2B)	1.891729	-25.68916338	0.043413
C(2)-O(1)	1.584842	-5.800409573	0.024088
C(1')-C(2')	2.177589	-19.58556696	0.394534
C(1')-H(1')	1.885541	-25.98430124	0.042539
C(1')-N(2')	2.118089	-22.35008352	0.144236
C(2')-H(2')	1.888875	-26.43747895	0.042099
C(2')-N(1')	2.036501	-14.54745025	0.149919
C(3)-C(4)	1.7957	-15.80451532	0.143287
C(3)-O(1)	2.08897	-8.969544784	0.008429
C(3)-O(2)	2.797363	6.006622902	0.093513

C(3')-C(4')	1.753226	-15.25491837	0.050699
C(3')-N(1')	2.175375	-17.63464958	0.198231
C(3')-N(2')	2.411473	-26.1222186	0.271184
C(4')-H(4'A)	1.84277	-24.21282344	0.007494
C(4')-H(4'B)	1.824333	-23.62208985	0.010255
C(4')-H(4'C)	1.825528	-23.64985165	0.010101
C(4)-C(5)	1.856564	-16.41660044	0.16728
C(4)-C(8)	2.170557	-19.731943	0.277119
C(5)-O(3)	2.836679	6.133695811	0.120301
C(5)-O(4)	1.850423	-8.984606527	0.047296
C(6)-C(7)	2.057104	-18.799344	0.232204
C(6)-C(9)	2.10744	-19.49037675	0.289022
C(6)-O(4)	1.911785	-3.739529423	0.049952
C(7)-C(12)	1.999527	-17.66183301	0.181263
C(7)-C(8)	1.972223	-17.68229288	0.12747
C(8)-H(8)	1.908721	-27.2297507	0.008675
C(9)-C(10)	2.064426	-18.85648223	0.251596
C(9)-H(9)	1.857954	-24.84994719	0.027085
H(5)-N(2')	0.442097	2.985695237	0.026359
H(11)-N(2')	0.058238	0.68953862	0.751683
N(1')-H(1'A)	2.220441	-39.82534372	0.027102
O(1)-H(8)	0.111921	1.950941479	4.635021
O(2)-O(3)	0.087162	1.026632466	0.362979
O(5)-H(5)	1.936592	-42.82190751	0.013597

Table S.26: List of ring critical points (RCP's) found from topological analysis of the theoretical ground state of 3.a

Atoms	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})
O(2)-O(3)-C(5)-C(4)-C(3)	0.012433	0.058344
C(3)-C(4)-C(8)-H(8)-O(1)	0.016577	0.087325
C(1')-C(2')-N(1')-C(3')-N(2')	0.055187	0.456508
C(4)-C(5)-O(4)-C(6)-C(7)-C(8)	0.020513	0.156593
C(6)-C(7)-C(12)-C(11)-C(10)-C()	0.019991	0.166468
C(10)-C(11)-N(2)-H(5)-O(5)	0.008257	0.035847

Table S.27: Atomic charges (e) from the theoretical ground state of 3.a

Name	Ω
C(1)	0.141529
C(10)	0.673946
C(11)	-0.01192

C(12)	0.02172
C(2)	0.536939
C(1')	0.467916
C(2')	0.421911
C(3)	1.683047
C(3')	1.136017
C(4')	0.12856
C(4)	-0.02872
C(5)	1.591856
C(6)	0.521508
C(7)	0.000976
C(8)	0.027906
C(9)	0.006187
H(1A)	-0.02418
H(1B)	-0.01618
H(1C)	-0.02397
H(2B)	0.004028
H(2A)	0.002017
H(5)	0.677542
H(8)	0.089442
H(9)	0.042461
H(11)	0.030105
H(12)	0.036187
H(1')	0.039431
H(2')	0.075278
H(1'A)	0.544476
H(4'A)	0.013456
H(4'B)	0.008429
H(4'C)	0.007927
N(1')	-1.39832
N(2')	-1.33979
O(1)	-1.15654
O(2)	-1.25034
O(3)	-1.2456
O(4)	-1.15554
O(5)	-1.28002
-----	-0.00033

Table S.28: List of bond critical points (BCP's) found from topological analysis of the theoretical first excited state of 3.a

Bond	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})	ε
C(1)-C(2)	1.719781361	-14.86169844	0.036991
C(1)-H(1A)	1.82637818	-23.38086098	0.006385
C(1)-H(1B)	1.824616862	-23.41375582	0.004853

C(1)-H(1C)	1.826857312	-23.39529615	0.006418
C(10)-C(11)	1.94473736	-17.26555254	0.182277
C(10)-O(5)	2.26313091	-5.258427832	0.027359
C(11)-C(12)	2.154914489	-19.69430069	0.27753
C(11)-H(11)	1.866699526	-25.05247341	0.023778
C(12)-C(12)	1.884609628	-25.87800149	0.004031
C(2)-H(2A)	1.88521023	-25.42716136	0.043501
C(2)-H(2B)	1.889104024	-25.565633	0.042415
C(2)-O(1)	1.618718182	-5.940399432	0.023299
C(1')-C(2')	2.184573455	-19.70287986	0.396789
C(1')-H(1')	1.888969057	-26.22584339	0.041528
C(1')-N(2')	2.102419132	-21.52812206	0.142988
C(2')-H(2')	1.891621156	-26.60730311	0.041255
C(2')-N(1')	2.034625283	-14.55518596	0.146741
C(3)-C(4)	1.86290021	-16.70679805	0.169952
C(3)-O(1)	2.026743219	-10.40783275	0.014286
C(3)-O(2)	2.742715371	3.238612017	0.090652
C(3')-C(4')	1.752389352	-15.24903826	0.04912
C(3')-N(1')	2.192981889	-17.95260899	0.200002
C(3')-N(2')	2.39236167	-25.52483375	0.265656
C(4')-H(4'A)	1.845739174	-24.33163046	0.008011
C(4')-H(4'B)	1.827228471	-23.75183772	0.010668
C(4')-H(4'C)	1.825811319	-23.70961664	0.010754
C(4)-C(5)	1.905219066	-17.02263676	0.199037
C(4)-C(8)	1.927394119	-15.7294958	0.24897
C(5)-O(3)	2.802195263	4.276329925	0.118862
C(5)-O(4)	1.78016553	-10.13667318	0.046431
C(6)-C(7)	1.914518282	-16.55837361	0.207283
C(6)-C(9)	2.175766868	-20.72580111	0.308153
C(6)-O(4)	1.918202877	-5.364968573	0.05074
C(7)-C(12)	1.903808662	-16.20245861	0.167406
C(7)-C(8)	2.048817047	-18.71914324	0.1642
C(8)-H(8)	1.926192915	-27.91803619	0.009323
C(9)-C(10)	1.983412111	-17.60850239	0.228549
C(9)-H(9)	1.855436543	-24.72952555	0.029335
H(5)-N(2')	0.691556649	0.088346157	0.024351
H(11)-N(2')	0.05260333	0.728289471	5.206854
N(1')-H(1'A)	2.217086969	-39.92352218	0.026546
O(2)-O(3)	1.568179845	-21.52850764	0.012779
O(5)-H(5)	1.568179845	-21.52850764	0.012779

Table S.29: List of ring critical points (RCP's) found from topological analysis of the theoretical excited state of 3.a

Atoms		ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ$^-$

		5)
O(2)-O(3)-C(5)-C(4)-C(3)	0.012466	0.056619
C(1')-C(2')-N(1')-C(3')-N(2')	0.054928	0.457592
C(4)-C(5)-O(4)-C(6)-C(7)-C(8)	0.019405	0.145464
C(6)-C(7)-C(12)-C(11)-C(10)-C()	0.018972	0.156254
C(10)-C(11)-N(2)-H(5)-O(5)	0.00779	0.032429

Table S.30: Atomic charges (e) from the theoretical excited state of 3.a

Name	Ω
C(1)	0.140727
C(10)	0.744104
C(11)	-0.01527
C(12)	0.018387
C(2)	0.553484
C(1')	0.466074
C(2')	0.427931
C(3)	1.633472
C(3')	1.140035
C(4')	0.129444
C(4)	-0.04033
C(5)	1.539047
C(6)	0.523994
C(7)	-0.00923
C(8)	0.028522
C(9)	0.003147
H(1A)	-0.02619
H(1B)	-0.01831
H(1C)	-0.02601
H(2B)	-0.00475
H(2A)	-0.00155
H(5)	0.658854
H(8)	0.100683
H(9)	0.039275
H(11)	0.02854
H(12)	0.03902
H(1')	0.05223
H(2')	0.082537
H(1'A)	0.548877
H(4'A)	0.018646
H(4'B)	0.01365
H(4'C)	0.013572
N(1')	-1.39687
N(2')	-1.34738
O(1)	-1.15182

O(2)	-1.24567
O(3)	-1.24694
O(4)	-1.13406
O(5)	-1.28047
-----	-0.0006

Optimised Cartesian coordinates of the excitoplex states of (3).

3.a-excitoplex

atom	X	y	Z
C	9.98676332546737	11.58695376685175	13.14680593427348
C	9.70153872829219	10.10480322414775	13.19084258281470
C	8.61703660489450	8.47885944429647	11.86396039299769
C	7.82504794629202	8.26463547203611	10.63047040977618
C	7.38345421087111	6.91710217128968	10.28241519776672
C	6.35711621214456	7.82891322047340	8.28051858063369
C	6.76409185894697	9.14141144611965	8.61558170178095
C	7.50085408732063	9.31789052616399	9.80381862108702
C	5.64678176760991	7.54433251916397	7.13177480036592
C	5.29671188104346	8.58666010065836	6.22285597558928
C	5.70470933461262	9.92938195616786	6.57341163605475
C	6.40869376134550	10.18555499391583	7.71981447842594
O	8.92810735183303	9.77010675777479	12.03394762650052
O	8.96722540045185	7.62551758589281	12.64798345859208
O	7.56077400621308	5.89180634070262	10.89300529272189
O	6.67264881581080	6.80008041793791	9.10771381300543
O	4.65159057268031	8.33140938126124	5.15135572029487
H	10.56023450090091	11.84927243049854	12.24558413978632
H	10.57702152642254	11.87687148176433	14.02782917555010
H	9.05269691763227	12.16758012154291	13.14951938220062
H	10.62833038697782	9.51014283471977	13.18616398660721
H	9.13414230185201	9.82368547711632	14.09214661240386

H	7.82940411393871	10.32344219650890	10.07781382793088
H	5.35811066631311	6.51625152998596	6.90488744220604
H	5.43914521921291	10.74623559096549	5.89765327497428
H	6.70881289971792	11.20839161167250	7.96624110650631
C	5.28658607377667	10.36746848241809	2.27028085050895
C	4.77997837867971	11.44478088673833	1.60762767072669
C	3.47710001474415	11.01199319780438	3.35215007433040
C	2.39508118201845	11.09632658409716	4.36566566328956
N	3.65324069169587	11.82522939421259	2.30195271363282
N	4.46063347656706	10.12040536211734	3.34288304802706
H	6.16265172358702	9.75849311359194	2.06283365443458
H	5.11492102247831	11.96690592926822	0.71556876518512
H	3.04445032324045	12.60316909135573	2.06255475286766
H	2.43471492618899	10.20849053053198	5.00805651958876
H	1.41232734223167	11.15047197684864	3.87806647067697
H	2.52445980117714	11.99366411759689	4.98790166397925
H	4.57224364481599	9.33710473378909	4.12389898190493

3.c-excitoplex

atom	X	y	Z
O	2.45108101793189	2.65883294454623	-1.46497550642096
O	1.45295603411407	4.65072834423945	-1.61053992789009
O	2.11753994558804	6.42528216247906	0.52723159713051
O	3.47221545291717	5.64288337443785	2.06324463898752
O	6.24747338774125	4.27861501109985	5.62102883295593
C	2.16033204074441	0.80158215243145	-2.91522952258335
C	1.75850207080193	2.23124756324068	-2.63886971204664
C	2.20772340647030	3.90440873682817	-1.02395201032978
C	2.94307813858013	4.19198494374006	0.22011880979546
C	2.78083707308452	5.47709403459094	0.87804119843965
C	4.26371702388375	4.70457919217325	2.64958132371750

C	4.43564580888566	3.44743733674319	2.00236632719789
C	3.76832735774455	3.23506360776911	0.79602442743862
C	4.85491124581043	5.00514642768564	3.85092283212782
C	5.69062028985377	4.03818329745838	4.53401952729399
C	5.84117828137171	2.74347286787634	3.86103070448723
C	5.25176236352850	2.47599287590851	2.66236031507709
H	1.89379940694633	0.14946615506894	-2.07028372520527
H	1.64312671948648	0.43375349038451	-3.81291750075707
H	3.24444703556649	0.72495603473515	-3.08497746407047
H	0.67398664634125	2.32556174684483	-2.46933728952524
H	2.01952047102508	2.89789385870756	-3.47594028230347
H	3.87986860374586	2.27143673501639	0.29200722121749
H	4.69570688749043	5.98270943913257	4.31168096122503
H	6.46018743705281	1.99592558863113	4.36541819330526
H	5.38318999871604	1.50150219236524	2.18112193828557
N	0.65398035034318	2.22855434385867	1.85480535633501
N	2.05784586628143	0.82538084985465	2.64717352707453
C	1.61505095496400	0.30036281723081	1.45142850889710
C	0.72179846844519	1.19309946928883	0.94825987334094
C	1.47245236061263	2.00037012562200	2.88294855297633
C	1.66869607425816	2.86599184925133	4.06874387887008
H	1.97618710756954	-0.64863170270026	1.06562591355404
H	0.14095208317566	1.18828681961112	0.03047037934231
H	0.08075609523295	3.06324792506625	1.75566381147605
H	0.97259326049758	2.57050445297125	4.86772793933183
H	1.47661111785808	3.91286354274639	3.80263716279047
H	2.69713769831388	2.76861599008334	4.44029947970957
H	2.74405743702474	0.39725489298106	3.26479672875145

Melting Point Testing of Crystals

The melting points of (1), (2) and (3) were obtained using a Stanford Research Systems, OptiMelt. The crystals were placed in a glass capillary tube and the melting point range was set from $50^{\circ}C$ to $250^{\circ}C$ using a $6^{\circ}C$/min gradient.

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