STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 73 (2017)

Supporting information for article:

Synthesis and crystal structure of pyrroloquinoline quinol (PQQH2) and pyrroloquinoline quinone (PQQ)

Kazuto Ikemoto, Shigeki Mori and Kazuo Mukai

Table S1 Crystallographic refinement data for $PQQH_2 \cdot 2DMSO \cdot CH_3CN$ and PQQ·3DMSO.

	$PQQH_2 \cdot 2DMSO \cdot CH_3CN$	PQQ·3DMSO
Empirical Formula	$C_{20}H_{23}N_3O_{10}S_2$	$C_{20}H_{24}N_2O_{11}S_3$
Formula Weight	529.54	564.60
Crystal Color, Habit	orange, needle	orange, block
Crystal Dimensions	0.240 × 0.030 × 0.020 mm	0.050 × 0.050 × 0.020 mm
Crystal System	orthorhombic	orthorhombic
Lattice Type	Primitive	Primitive
Lattice Parameters	a = 14.563(5) Å	a = 6.901(5) Å
	b = 6.748(2) Å	b = 12.371(8) Å
	c = 23.299(9) Å	c = 28.674(18) Å
	V = 2289.6(14) $Å^3$	V = 2448(3) $Å^3$
Space Group	Pnma (#62)	$P2_12_12_1$ (#19)
Z value	4	4
D_{calc}	1.536 g/cm^3	1.532 g/cm^3
F_{000}	1104.00	1176.00
	2.954 cm^{-1}	3.654 cm^-
1176.00	0.0602	1
μ	0.1343	
(MoKα)		3.654 cm^{-1}
		0.0698
3.654 cm^{-1}		0.1857
R1 [$I > 2\sigma(I)$]		
wR2 [all data]		

Table S2 Torsion angles (Selected) (º) of $PQQH_2$ molecule in $PQQH_2$•2DMSO•CH_3CN single crystal.

atom1	atom2	atom3	atom4	angle/deg	atom1	atom2	atom3	atom4	angle/deg
C2	N1	C1A	C9A	180.0	C2	N1	C1A	C3A	0.0
C1A	N1	C2	C3	0.0	C1A	N1	C2	C10	180.0
N1	C2	C3	C3A	0.0	N1	C2	C10	O2	180.0
C10	C2	C3	C3A	180.0	C8	C7	C11	O5	0.0
C2	C3	C3A	C4	180.0	C2	C3	C3A	C1A	0.0
O3	C4	C5	O4	0.0	O3	C4	C5	C5A	180.0
O3	C4	C3A	C3	0.0	O3	C4	C3A	C1A	180.0
C5	C4	C3A	C3	180.0	C5	C4	C3A	C1A	0.0
C3A	C4	C5	O4	180.0	C3A	C4	C5	C5A	0.0
O4	C5	C5A	N6	0.0	O4	C5	C5A	C9A	180.0
C4	C5	C5A	N6	180.0	C4	C5	C5A	C9A	0.0
C11	C7	C8	C9	180.0	C8	C7	N6	C5A	0.0
N6	C7	C8	C9	0.0	C11	C7	N6	C5A	180.0
C7	C8	C9	C12	180.0	C7	C8	C9	C9A	0.0
C8	C9	C12	O7	180.0	C9A	C1A	C3A	C4	0.0
C8	C9	C9A	C1A	180.0	C8	C9	C9A	C5A	0.0
C12	C9	C9A	C1A	0.0	C12	C9	C9A	C5A	180.0
C7	N6	C5A	C5	180.0	C7	N6	C5A	C9A	0.0
C9	C9A	C1A	N1	0.0	C9	C9A	C1A	C3A	180.0
C9	C9A	C5A	C5	180.0	C9	C9A	C5A	N6	0.0
C1A	C9A	C5A	C5	0.0	C1A	C9A	C5A	N6	180.0

C5A	C9A	C1A	N1	180.0	C5A	C9A	C1A	C3A	0.0
N1	C1A	C3A	C3	0.0	N1	C1A	C3A	C4	180.0
C9A	C1A	C3A	C3	180.0					

Table S3 Possible hydrogen bonds in $PQQH_2$•2DMSO•CH_3CN single crystal.

Donor	H	Acceptor	D...A/Å	D-H/Å	H...A/Å	D-H...A/deg	
O2	H2O	O2S [a, b]	2.722(3)	0.81	1.91	175.39	
O2	H2O	O3S [a]	2.722(3)	0.81	1.91	175.39	
O2	H2O	O4S [a]	2.722(3)	0.81	1.91	175.39	
O3	H3O	O4	2.739(3)	0.94	2.25	111.76	intramol. [c]
O3	H3O	N1S	2.925(4)	0.94	2.06	153.63	
O4	H4O	N6	2.681(3)	0.77	2.30	111.54	intramol.
O4	H4O	O1S	2.716(3)	0.77	1.97	162.96	
O6	H6O	N6	2.711(3)	0.91	2.25	110.90	intramol.
O6	H6O	O1S	2.650(3)	0.91	1.78	157.38	
N1	H1N	O7	2.628(3)	0.88	1.87	144.49	intramol.
O8	H8O	O2S [a]	2.677(3)	0.86	1.83	169.43	
O8	H8O	O3S [a]	2.677(3)	0.86	1.83	169.43	
O8	H8O	O4S [a]	2.677(3)	0.86	1.83	169.43	

[a] One of two DMSO molecules included in $PQQH_2$·2DMSO·CH_3CN showed a disorder in the crystal, as shown in Fig. S1. Optimization of the orientation of the DMSO molecule was performed, and, at least, three kinds of different conformations were observed for one DMSO molecule.

[b] "S" in O1S, O2S, O3S, O4S, and N1S is abbreviation of "solvent".

[c] "intramol." is abbreviation of "intra molecular hydrogen bond".

Table S4 Torsion angles (°) of PQQ molecule in PQQ•3DMSO single crystal.

atom1	atom2	atom3	atom4	angle/deg	atom1	atom2	atom3	atom4	angle/deg
C2	N1	C1A	C3A	0.4(6)	C2	N1	C1A	C9A	176.4(5)
C1A	N1	C2	C3	-0.3(6)	C1A	N1	C2	C10	178.9(4)
N1	C2	C3	C3A	0.1(6)	N1	C2	C10	O1	-4.1(9)
N1	C2	C10	O2	176.6(5)	C3	C2	C10	O1	175.0(6)
C3	C2	C10	O2	-4.3(10)	C10	C2	C3	C3A	-179.0(6)
C2	C3	C3A	C1A	0.1(6)	C2	C3	C3A	C4	176.5(5)
O4	C5	C5A	N6	11.2(8)	O4	C5	C5A	C9A	-171.2(5)
O4	C5	C4	O3	-9.2(8)	O4	C5	C4	C3A	169.6(5)
C5A	C5	C4	O3	171.7(5)	C5A	C5	C4	C3A	-9.5(7)
C4	C5	C5A	N6	-169.7(4)	C4	C5	C5A	C9A	7.8(7)
C8	C7	C11	O5	171.5(5)	C8	C7	C11	O6	-7.2(8)
C11	C7	C8	C9	-178.7(4)	C8	C7	N6	C5A	0.5(8)
N6	C7	C8	C9	2.7(8)	C11	C7	N6	C5A	-178.1(4)
N6	C7	C11	O5	-9.9(8)	N6	C7	C11	O6	171.5(5)
C7	C8	C9	C12	175.4(4)	C7	C8	C9	C9A	-3.8(8)
C8	C9	C12	O7	-143.3(5)	C8	C9	C12	O8	33.0(7)
C8	C9	C9A	C5A	1.8(7)	C8	C9	C9A	C1A	-174.8(5)
C12	C9	C9A	C5A	-177.2(5)	C12	C9	C9A	C1A	6.2(9)
C9A	C9	C12	O7	35.7(8)	C9A	C9	C12	O8	-148.0(5)

C3	C3A	C1A	N1	-0.3(6)	C3	C3A	C1A	C9A	-176.5(5)
C3	C3A	C4	O3	5.3(10)	C3	C3A	C4	C5	-173.3(5)
C1A	C3A	C4	O3	-178.7(5)	C1A	C3A	C4	C5	2.6(8)
C4	C3A	C1A	N1	-177.0(5)	C4	C3A	C1A	C9A	6.8(9)
C5	C5A	N6	C7	174.9(4)	C5	C5A	C9A	C9	-175.9(4)
C5	C5A	C9A	C1A	1.1(7)	N6	C5A	C9A	C9	1.4(8)
N6	C5A	C9A	C1A	178.4(5)	C9A	C5A	N6	C7	-2.6(8)
C9	C9A	C1A	N1	-7.5(9)	C9	C9A	C1A	C3A	167.9(5)
C5A	C9A	C1A	N1	175.9(5)	C5A	C9A	C1A	C3A	-8.8(8)

Table S5 Possible hydrogen bonds in PQQ•3DMSO single crystal.

Donor	H	Acceptor	D...A/Å	D-H/Å	H...A/Å	D-H...A/deg	
O2	H2O	O1S [a]	2.593(6)	0.84	1.75	178.87	
O6	H6O	O2S	2.554(6)	0.84	1.72	171.33	
O8	H8O	O3S	2.431(6)	0.84	1.63	157.52	
N1	H1N	O1	2.767(7)	0.96	2.58	90.61	intramol. [b]
N1	H1N	O7	2.673(6)	0.96	1.83	144.97	intramol.

[a] "S" in O1S, O2S, and O3S is abbreviation of "solvent".

[b] "intramol." is abbreviation of "intra molecular hydrogen bond".

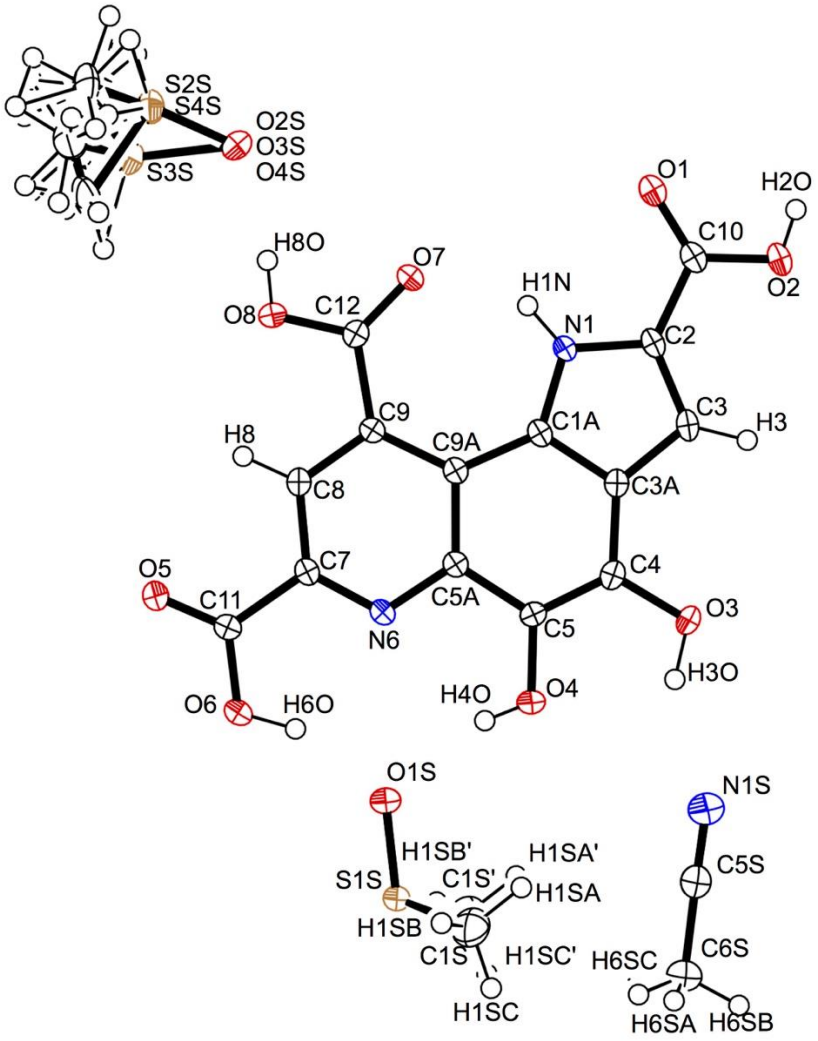

Figure S1 Molecular structure of $PQQH_2 \cdot 2DMSO \cdot CH_3CN$. Thermal ellipsoids of C, N, O, and S are set at 50% probability. One of two DMSO molecules included in $PQQH_2 \cdot 2DMSO \cdot CH_3CN$ showed a disorder in the crystal. Atomic numbering for methyl groups of disordered DMSO molecules is omitted for clarity. Optimization of the orientation of the DMSO molecule was performed, and, at least, three kinds of different conformations were observed for one DMSO molecule (see Table S3).

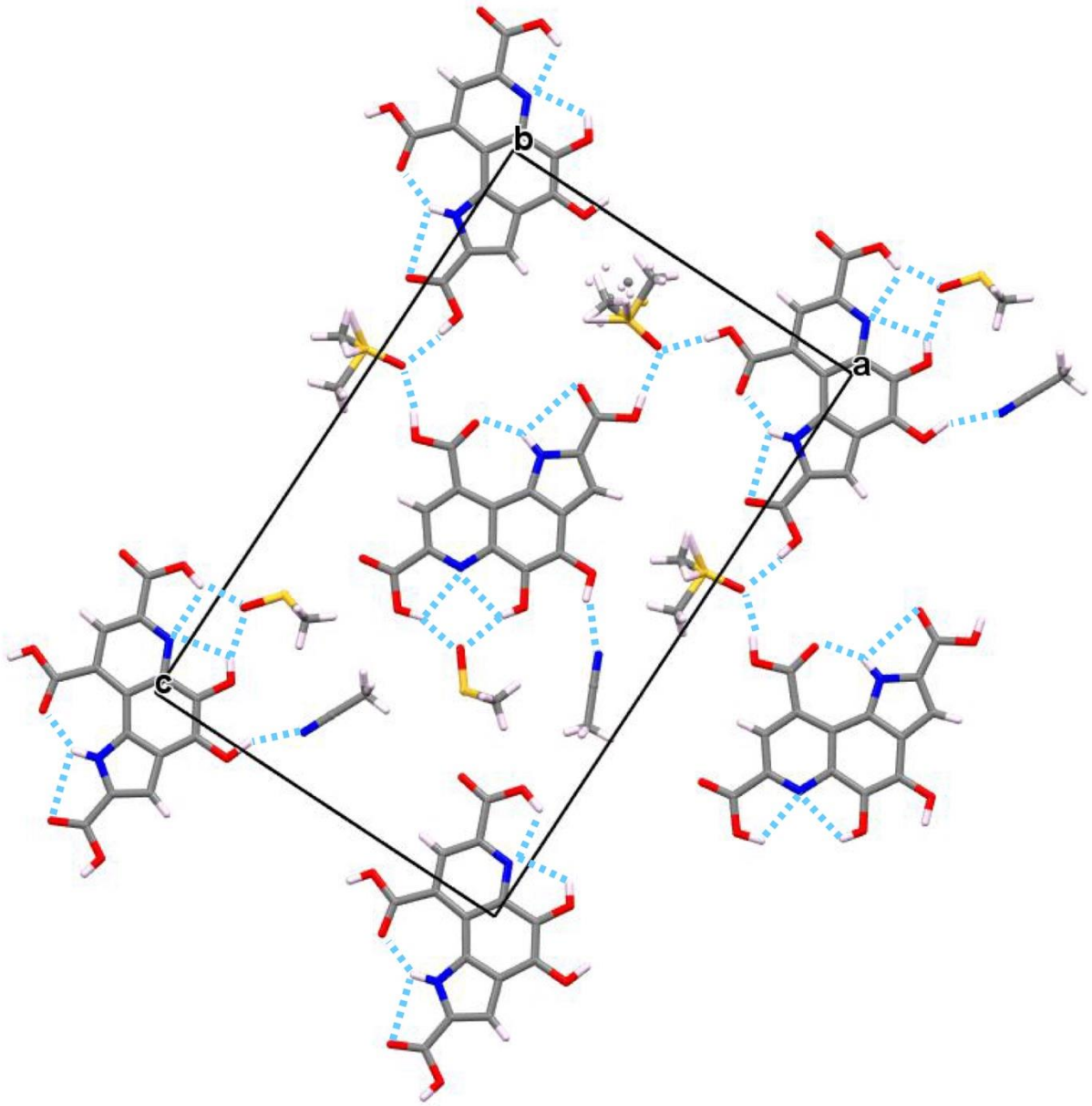

Figure S2 Crystal structure of $PQQH_2 \cdot 2DMSO \cdot CH_3CN$. View from the top; the intra and inter molecular hydrogen bonds are marked as dashed lines (see Table S3). $PQQH_2$ molecule is surrounded by four DMSO and one CH_3CN molecules, forming hydrogen bonds, respectively.