

1,1',3,3'-Tetramesitylquinobis(imidazole)-2,2'-dithione

Jayaraman Selvakumar and Kuppaswamy Arumugam*

Department of Chemistry, Wright State University, 3640 Colonel Glenn Hwy, Dayton, OH 45435, USA.

*Correspondence e-mail: kuppaswamy.arumugam@wright.edu

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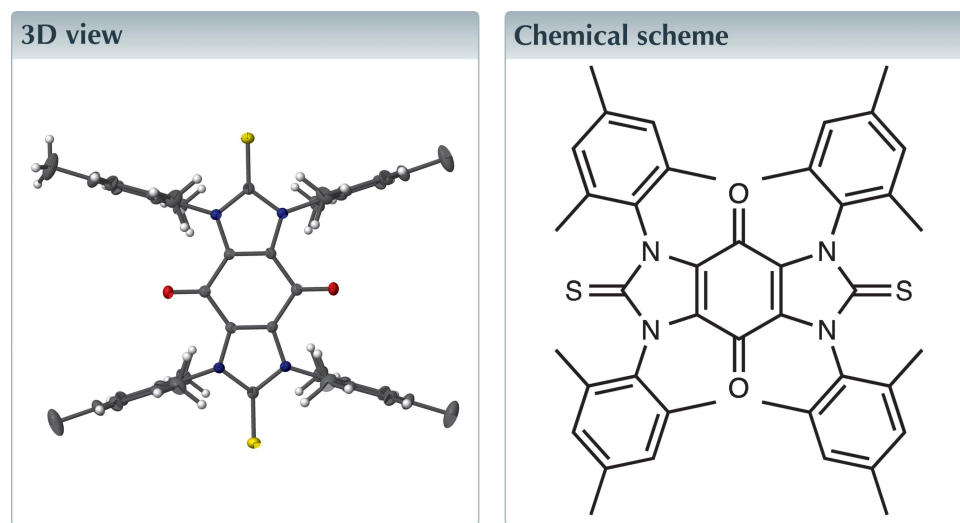
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Structural data: full structural data are available from iucrdata.iucr.org

The solid-state structural analysis of the title compound [systematic name: 5,11-disulfanylidene-4,6,10,12-tetrakis(2,4,6-trimethylphenyl)-4,6,10,12-tetraazatriacyclo[7.3.0.0.3⁷]dodeca-1(9),3(7)-diene-2,8-dione], $C_{44}H_{44}N_4O_2S_2$ [+solvent], reveals that the molecule crystallizes in a highly symmetric cubic space group so that one quarter of the molecule is crystallographically unique, the molecule lying on special positions (two mirror planes, two twofold axes and a center of inversion). The crystal structure exhibits large cavities of 193 \AA^3 accounting for 7.3% of the total unit-cell volume. These cavities contain residual density peaks but it was not possible to unambiguously identify the solvent therein. The contribution of the disordered solvent molecules to the scattering was removed using a solvent mask and is not included in the reported molecular weight. No classical hydrogen bonds are observed between the main molecules.



Structure description

A variety of substituted imidazole-2-thiones have been synthesized and used as precursors for the generation of free *N*-heterocyclic carbenes (Kuhn & Kratz, 1993). Other uses for these types of molecules include the stabilization of gold nanoparticles (Moraes *et al.*, 2017; Okamoto *et al.*, 2006) and as ligands for metal coordination studies (Parveen *et al.*, 2019). As part of our ongoing effort with bis(*N*-heterocyclic carbene) and its transition-metal complexes (Tennyson *et al.*, 2010), the title compound (1,1',3,3'-tetramesitylquinobis(imidazole)-2,2'-dithione) was synthesized and its single-crystal X-ray analysis is reported here.

The molecular structure of the title compound is presented in Fig. 1. The molecules crystallize in a rare cubic space group ($Im\bar{3}$) with $Z = 6$ and lie on special positions (two mirror planes, two twofold axes and a center of inversion). A search in the Cambridge Structural Database revealed that only 0.3% of the crystals were reported to crystallize in

the $Im\bar{3}$ space group. Three imidazolidine-thione structures closely related to the title compound were reported: 1-methyl-3-phenylimidazolidine-2-thione (Nor *et al.*, 2014), 1,3-dibenzylimidazolidine-2-thione (Mietlarek-Kropidłowska *et al.*, 2012), and 7-amino-1,2,3,4-tetrahydroquinazoline-2,4-dithione, (Yang *et al.*, 2006). The C1–S1 bond distance of 1.659 (3) Å falls well within the range observed for other reported thione-type compounds (1.653–1.686 Å). The N1–C1–N1' bond angle of 105.3 (3)° is also very similar to those reported in other thione-type compounds (108–116°). The imidazole and mesityl rings are found to be perpendicular to each other. The two imidazole rings that are on the opposite side of the quino-bis(imidazolidine)dithione share the same plane with the mesityl units oriented perpendicular to it.

The crystal structure exhibits large cavities of 193 Å³ accounting for 7.3% of the total unit-cell volume of 5933.5 (11) Å³ (Fig. 2) These cavities contain residual density peaks but it was not possible to unambiguously identify the solvent therein. The contribution of the disordered solvent molecules to the scattering was removed using the solvent mask in OLEX2 (Dolomanov *et al.*, 2009) and was not included in the reported molecular weight. No classical hydrogen bonds are observed between the main molecules.

Synthesis and crystallization

To the stirred solution of 1,1',3,3'-tetramesitylquinobis(imidazole) dichloride (73 mg, 1 mmol) (Tennyson *et al.*, 2010)

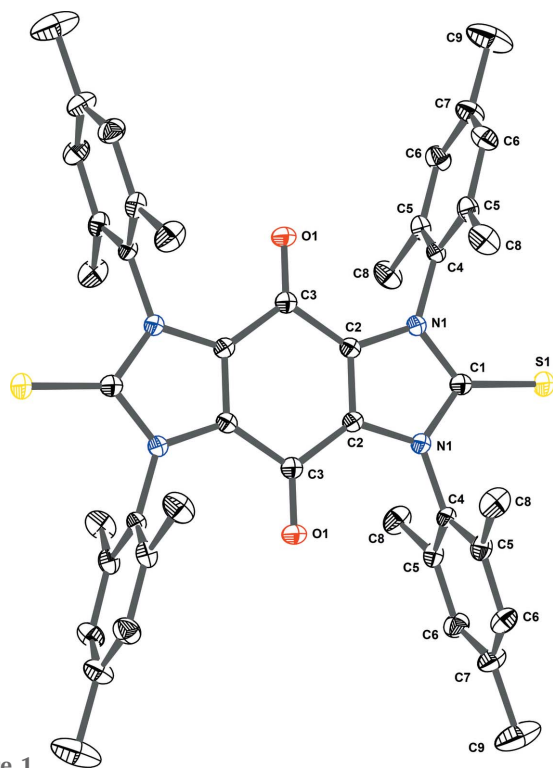


Figure 1
Molecular structure of the title compound with atom labeling. Displacement ellipsoids are drawn at the 50% probability level and all hydrogen atoms are omitted for clarity. Unlabeled atoms are generated by the symmetry operation $(-x, -y, z)$, $(-x, y, -z)$ and $(x, -y, -z)$.

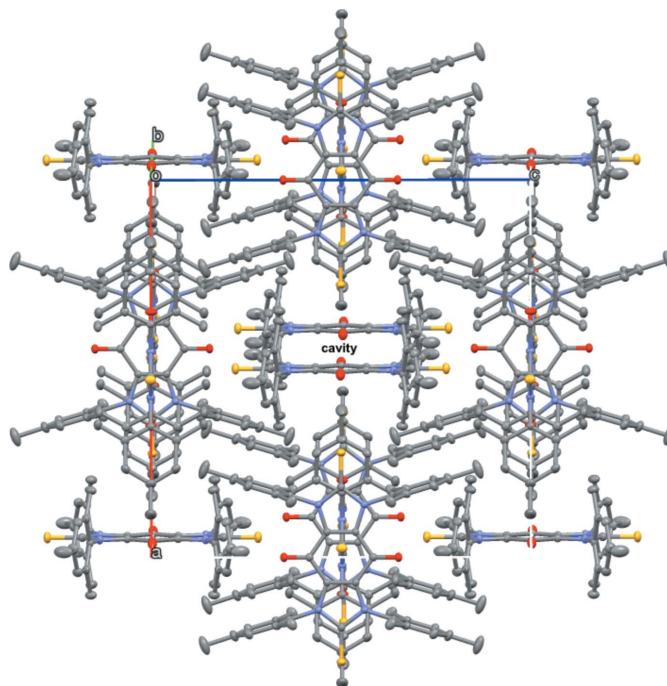


Figure 2
A three-dimensional packing diagram of the title compound viewed along the *b* axis.

in THF (10 mL), $\text{NaN}(\text{Si}(\text{CH}_3)_3)_2$ (40 mg, 2.2 mmol) in THF (2 mL) was added drop wise at 25°C. After stirring for 60 min, elemental sulfur (76 mg, 2.4 mmol) was added as a solid and the solution was stirred for another 60 min. The resulting reaction mixture was filtered through a celite plug and the volatiles were removed under vacuum. The resulting residue was dissolved in a minimum amount of dichloromethane (3 ml) and precipitated with hexane (15 mL) to yield 1,1',3,3'-tetramesitylquinobis(imidazole)-2,2'-dithione as a fine yellow solid: 62 mg, 85% yield. Black-colored diffraction-quality single crystals were obtained by diffusing hexane into a saturated solution of the title compound in 1,2-dichloroethane. FT-IR (NaCl): 3027, 2974, 2917, 2850, 1672, 1546, 1397, 1321, 1286, 1042, 1033, 849, 612; ¹H NMR (CDCl_3 , 300 MHz): δ 6.98 (s, 8H), 2.31 (s, 12H), 2.07 (s, 24H); ¹³C NMR (CDCl_3 , 75 MHz): δ 169.31, 163.93, 139.70, 134.59, 131.24, 129.77, 126.78, 21.33, 21.97.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. A solvent mask was generated revealing voids at (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with a volume of 192.6 Å³ and containing about 43 electrons. The solvent could not be unambiguously identified.

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Table 1
Experimental details.

Crystal data	
Chemical formula	C ₄₄ H ₄₄ N ₄ O ₂ S ₂
<i>M_r</i>	724.98
Crystal system, space group	Cubic, <i>Im</i> $\bar{3}$
Temperature (K)	100
<i>a</i> (Å)	18.1038 (11)
<i>V</i> (Å ³)	5933.5 (11)
<i>Z</i>	6
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	0.18
Crystal size (mm)	0.25 × 0.15 × 0.1
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2016)
<i>T_{min}</i> , <i>T_{max}</i>	0.969, 0.983
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	82590, 1249, 1074
<i>R_{int}</i>	0.035
(sin θ/λ) _{max} (Å ⁻¹)	0.649
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.049, 0.122, 1.11
No. of reflections	1246
No. of parameters	76
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.49, -0.33

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

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full crystallographic data

IUCrData (2019). 4, x191268 [https://doi.org/10.1107/S2414314619012689]

1,1',3,3'-Tetramesitylquinobis(imidazole)-2,2'-dithione

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5,11-Disulfanylidene-4,6,10,12-tetrakis(2,4,6-trimethylphenyl)-4,6,10,12-tetraazatricyclo[7.3.0.0^(3,7)]dodeca-1(9),3(7)-diene-2,8-dione [+solvent]

Crystal data

C₄₄H₄₄N₄O₂S₂

M_r = 724.98

Cubic, *Im*³

a = 18.1038 (11) Å

V = 5933.5 (11) Å³

Z = 6

F(000) = 2304

D_x = 1.217 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 9582 reflections

θ = 2.8–27.5°

μ = 0.18 mm⁻¹

T = 100 K

Needle, black

0.25 × 0.15 × 0.1 mm

Data collection

Bruker APEXII CCD

diffractometer

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2016)

T_{min} = 0.969, *T_{max}* = 0.983

82590 measured reflections

1249 independent reflections

1074 reflections with *I* > 2σ(*I*)

R_{int} = 0.035

θ_{max} = 27.5°, θ_{min} = 3.2°

h = −23→23

k = −23→23

l = −23→23

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.049

wR(*F*²) = 0.122

S = 1.11

1246 reflections

76 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0406*P*)² + 16.2491*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.49 e Å⁻³

Δρ_{min} = −0.33 e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Aromatic C–H hydrogen atoms were added as riding-model approximation with C–H bond length 0.95 Å. Methyl (CH₃) H atoms were treated as a rotating group and added as riding-model approximation to the carbon atom to which they are attached, the methyl H atoms were fixed at a distance of 0.98 Å with *U*_{iso}(H) = 1.5*U*_{eq}(CH₃).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.500000	1.000000	0.77751 (5)	0.0225 (2)	
O1	0.500000	0.84916 (13)	0.500000	0.0217 (5)	
N1	0.500000	0.93936 (10)	0.63961 (10)	0.0155 (4)	
C2	0.500000	0.96233 (12)	0.56706 (12)	0.0152 (4)	
C3	0.500000	0.91602 (17)	0.500000	0.0160 (6)	
C4	0.500000	0.86372 (12)	0.66431 (12)	0.0154 (4)	
C1	0.500000	1.000000	0.68589 (18)	0.0170 (6)	
C5	0.43245 (9)	0.82885 (9)	0.67454 (9)	0.0191 (4)	
C6	0.43410 (10)	0.75514 (10)	0.69637 (10)	0.0231 (4)	
H6	0.389700	0.730325	0.703546	0.028*	
C7	0.500000	0.71749 (14)	0.70777 (15)	0.0262 (6)	
C8	0.36117 (9)	0.86931 (10)	0.66228 (11)	0.0273 (4)	
H8B	0.358366	0.910622	0.695412	0.041*	
H8A	0.320463	0.836567	0.671379	0.041*	
H8C	0.359060	0.886643	0.612208	0.041*	
C9	0.500000	0.63900 (17)	0.7330 (2)	0.0495 (9)	
H9B	0.485357	0.636818	0.783948	0.074*	0.5
H9A	0.548719	0.618737	0.727763	0.074*	0.5
H9C	0.465923	0.610968	0.703621	0.074*	0.5

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0309 (5)	0.0219 (4)	0.0146 (4)	0.000	0.000	0.000
O1	0.0315 (13)	0.0132 (11)	0.0203 (12)	0.000	0.000	0.000
N1	0.0183 (9)	0.0148 (9)	0.0135 (9)	0.000	0.000	0.0005 (7)
C2	0.0154 (10)	0.0146 (11)	0.0155 (10)	0.000	0.000	0.0013 (8)
C3	0.0148 (14)	0.0163 (15)	0.0168 (14)	0.000	0.000	0.000
C4	0.0189 (10)	0.0148 (10)	0.0125 (10)	0.000	0.000	0.0019 (8)
C1	0.0177 (15)	0.0156 (14)	0.0177 (15)	0.000	0.000	0.000
C5	0.0196 (8)	0.0229 (8)	0.0149 (7)	0.0002 (6)	-0.0011 (6)	0.0023 (6)
C6	0.0225 (8)	0.0219 (8)	0.0250 (8)	-0.0051 (7)	-0.0004 (7)	0.0058 (7)
C7	0.0293 (13)	0.0202 (12)	0.0292 (13)	0.000	0.000	0.0082 (10)
C8	0.0179 (8)	0.0306 (9)	0.0334 (10)	0.0003 (7)	-0.0021 (7)	0.0081 (8)
C9	0.0341 (16)	0.0296 (15)	0.085 (3)	0.000	0.000	0.0253 (17)

Geometric parameters (\AA , $^\circ$)

S1—C1	1.659 (3)	C5—C8	1.500 (2)
O1—C3	1.210 (4)	C6—H6	0.9300
N1—C2	1.378 (3)	C6—C7	1.389 (2)
N1—C4	1.440 (3)	C7—C9	1.493 (4)
N1—C1	1.381 (3)	C8—H8B	0.9600
C2—C2 ⁱ	1.364 (4)	C8—H8A	0.9600
C2—C3	1.475 (3)	C8—H8C	0.9600

C4—C5	1.3886 (19)	C9—H9B	0.9600
C4—C5 ⁱⁱ	1.3886 (19)	C9—H9A	0.9600
C5—C6	1.392 (2)	C9—H9C	0.9600
C2—N1—C4	125.65 (18)	C5—C6—H6	119.0
C2—N1—C1	109.79 (19)	C7—C6—C5	122.06 (17)
C1—N1—C4	124.57 (19)	C7—C6—H6	119.0
N1—C2—C3	127.8 (2)	C6—C7—C6 ⁱⁱ	118.3 (2)
C2 ⁱ —C2—N1	107.56 (12)	C6 ⁱⁱ —C7—C9	120.83 (11)
C2 ⁱ —C2—C3	124.63 (13)	C6—C7—C9	120.83 (11)
O1—C3—C2	124.63 (13)	C5—C8—H8B	109.5
O1—C3—C2 ⁱⁱⁱ	124.63 (13)	C5—C8—H8A	109.5
C2 ⁱⁱⁱ —C3—C2	110.7 (3)	C5—C8—H8C	109.5
C5—C4—N1	118.27 (10)	H8B—C8—H8A	109.5
C5 ⁱⁱ —C4—N1	118.27 (10)	H8B—C8—H8C	109.5
C5—C4—C5 ⁱⁱ	123.4 (2)	H8A—C8—H8C	109.5
N1—C1—S1	127.35 (13)	C7—C9—H9B	109.5
N1 ⁱ —C1—S1	127.35 (13)	C7—C9—H9A	109.5
N1 ⁱ —C1—N1	105.3 (3)	C7—C9—H9C	109.5
C4—C5—C6	117.05 (16)	H9B—C9—H9A	109.5
C4—C5—C8	121.05 (15)	H9B—C9—H9C	109.5
C6—C5—C8	121.90 (15)	H9A—C9—H9C	109.5

Symmetry codes: (i) $-x+1, -y+2, z$; (ii) $-x+1, y, z$; (iii) $x, y, -z+1$.