

(7*Z*,7'*Z*)-2,2-Dimethyl-7,7'-(1,2,4-trithiolane-3,5-diylidene)bis[quinolin-8(7*H*)-one] chloroform disolvateJaroslaw Chojnacki,^{a*} Patrycja Skop,^b Agnieszka Pladzyk^a and Jacek E. Nycz^b^aChemical Faculty, Gdansk University of Technology, Narutowicza 11/12, PL-80952 Gdansk, Poland, and ^bDepartment of Organic Chemistry, University of Silesia, PL-40006 Katowice, Poland

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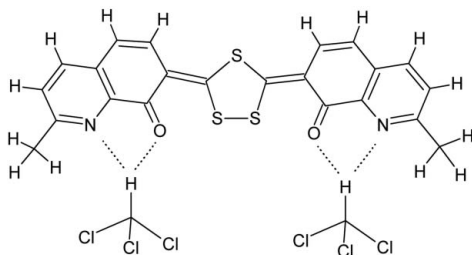
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Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.054; wR factor = 0.127; data-to-parameter ratio = 15.9.

The title compound, $\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_2\text{S}_3 \cdot 2\text{CHCl}_3$, was obtained unintentionally as the product of the reaction between the potassium salt of 8-hydroxy-2-methylquinoline-7-carbodithioic acid and $M[\text{OOC}(\text{CF}_3)_2]$ ($M = \text{Mg}, \text{Mn}$). Oxidation and sulfur elimination processes caused condensation of two acid molecules with the formation of an aromatic five-membered heterocycle S_3C_2 (trithiolane). The molecule shows local symmetry 2 (Schoenflies C_2) with the twofold rotation axis passing through the trithiolane ring. The two aromatic systems are essentially planar. The molecules possess the 7*Z*,7'*Z* conformation with respect to the unsaturated vinyl groups. The compound cocrystallizes with CHCl_3 , which is bound by weak bifurcated $\text{C}-\text{H} \cdots \text{O}(\text{N})$ hydrogen bonds. The packing of molecules in the structure is stabilized by $\pi-\pi$ stacking interactions.

Related literature

For the related structure 3,5-bis(2-tetralonylidene)-1,2,4-trithiole, see: Gonzalez-Castro *et al.* (2000). For related literature, see: Lee *et al.* (2005).

**Experimental***Crystal data* $\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_2\text{S}_3 \cdot 2\text{CHCl}_3$
 $M_r = 673.27$ Monoclinic, $C2/c$
 $a = 23.7359$ (13) Å
 $b = 10.6749$ (6) Å
 $c = 11.1128$ (6) Å
 $\beta = 104.149$ (5)° $V = 2730.3$ (3) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.89$ mm⁻¹ $T = 120$ (2) K $0.23 \times 0.11 \times 0.05$ mm*Data collection*

Oxford Diffraction KM4 CCD diffractometer

Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2006) $T_{\text{min}} = 0.867$, $T_{\text{max}} = 0.963$

9483 measured reflections

2682 independent reflections

2357 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.055$ *Refinement* $R[F^2 > 2\sigma(F^2)] = 0.054$ $wR(F^2) = 0.127$ $S = 1.12$

2682 reflections

169 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.59$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.40$ e Å⁻³**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{C3}-\text{H3} \cdots \text{S1}$	0.93	2.64	3.032 (3)	106
$\text{C12}-\text{H12} \cdots \text{O1}$	0.98	2.37	3.136 (4)	135
$\text{C12}-\text{H12} \cdots \text{N1}$	0.98	2.40	3.294 (4)	152

Table 2Main $\pi-\pi$ interactions (Å, °).

DA is the dihedral angle between the planes, DCC is the length of the CC vector (centroid-to-centroid), τ is the angle(s) subtended by the plane normal(s) to CC. Cg1 is the centroid of ring $\text{S1/C10/S2/S2'/C10'}$ and Cg2 is the centroid of ring $\text{C1}-\text{C5/C9}$.

Group 1	Group 2	DA	DCC	τ
Cg1	Cg2^{i}	3.62	3.650 (2)	16.31
Cg1	Cg2^{ii}	3.62	3.650 (2)	16.31

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999) and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2267).

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supplementary materials

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(7*Z*,7'*Z*)-2,2-Dimethyl-7,7'-(1,2,4-trithiolane-3,5-diylidene)bis[quinolin-8(7*H*)-one] chloroform disolvate

J. Chojnacki, P. Skop, A. Pladzyk and J. E. Nycz

Comment

The title compound, [C₂₂H₁₄N₂O₂S₃, 2(CHCl₃)], was obtained unintentionally as the product of the reactions between potassium salt of 8-hydroxy-2-methylquinoline-7-carbodithioic acid and M[OCCCF₃]₂ (M = Mg, Mn). Oxidation and sulfur elimination processes caused condensation of two acid molecules with the formation of aromatic five-membered heterocycle S₃C₂ (trithiolane). The mechanism of formation of the title compound is not fully recognized. Its structural novelty suggests considerable potential as functionalized ligand interesting in organometallic chemistry and it seems probable to be important as bioactive molecules. Naturally occurring trithiolanes (*e.g.* in garlic) significantly inhibited the formation of intracellular reactive oxygen species (Lee *et al.*, 2005). The heterocycle is stabilized by extended delocalization of electrons in conjugated aromatic systems. Molecules possess the (7*Z*,7'*Z*) conformation with respect to the unsaturated vinyls (C2—C10). The same product was obtained using Mg and Mn salt. In the related derivative, 3,5-bis(2-tetralonylidene)-1,2,4-trithiole, also *Z,Z'* conformation was determined (Gonzalez-Castro *et al.*, 2000). Valence angles on sulfur in (I) are close to the values reported there (99.74° for S—S—C and 103.02° for C—S—C). It seems that relatively acute angles on sulfur atoms (due to assumed lack of hybridization of sulfur orbitals) lead to the low tensed 5-membered ring, which explains the ease of formation of the central heterocycle.

C₂₂H₁₄N₂O₂S₃ molecule shows local symmetry 2 (Schoenflies C₂) with the twofold axis passing through the trithiolane ring. It is essentially planar, with root mean square deviation of atoms from the S1,S2,C1—C11,N1,O1 plane being only 0.0286 Å. Maximum deviation from the plane is shown by S2 atom and it is equal to -0.0594(0.0015) Å.

Packing of molecules in the structure is stabilized by π-π stacking interactions (see Table 2.). Compound cocrystallized with CHCl₃ which is bound by weak C—H...O(N) bifurcated hydrogen bonds.

Experimental

To the suspension of 8-hydroxy-2-methylquinoline-7-carbodithioic acid (2.350 g, 10.0 mmol) in H₂O (50 ml), K₂CO₃ (1.380 g, 10.0 mmol) was added and stirred up to the disappearance of the solid material. Subsequently, M[OCCCF₃] (M = Mg, Mn) (10.0 mmol) was slowly added. The reaction was carried out for 16 h at room temperature. Next the liquid reaction mixture was filtered off and the brown crude product was dried over P₂O₅. Final purification by crystallization from CHCl₃ gave material suitable for the *x*-ray structural analysis.

Refinement

All H atoms were treated as riding on their parent C atoms with methyl C—H = 0.96 Å, chloroform C—H = 0.98 Å, aromatic C—H = 0.93 Å and *U*_{iso}(H) = 1.2 *U*_{eq}(C) for aromatic CH and CHCl₃ and 1.5 for methyl groups. No disorder has been found.

Figures

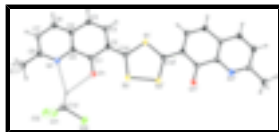


Fig. 1. View of (I) including the solvent linked through C—H \cdots O and C—H \cdots N hydrogen bonds with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

(7*Z*,7'*Z*)-2,2-Dimethyl-7,7'-(1,2,4-trithiolane-3,5-diylidene)bis[quinolin- 8(7*H*)-one] chloroform disolvate

Crystal data

C₂₂H₁₄N₂O₂S₃·2CHCl₃

M_r = 673.27

Monoclinic, *C*2/*c*

Hall symbol: -C 2yc

a = 23.7359 (13) Å

b = 10.6749 (6) Å

c = 11.1128 (6) Å

β = 104.149 (5)°

V = 2730.3 (3) Å³

Z = 4

*F*₀₀₀ = 1360

D_x = 1.638 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 6056 reflections

θ = 30.6–1.5°

μ = 0.89 mm⁻¹

T = 120 (2) K

Prism, red

0.23 × 0.11 × 0.05 mm

Data collection

KM4CCD, Oxford Diffraction diffractometer

Monochromator: graphite

T = 120 K

0.75° ω scans

Absorption correction: numerical (CrysAlis RED; Oxford Diffraction, 2006)

T_{min} = 0.867, *T_{max}* = 0.963

9483 measured reflections

2682 independent reflections

2357 reflections with *I* > 2σ(*I*)

R_{int} = 0.055

θ_{max} = 26°

θ_{min} = 2.1°

h = -29→29

k = -13→12

l = -13→12

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.054

wR (*F*²) = 0.127

S = 1.12

2682 reflections

169 parameters

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 10.8805P]$$

where *P* = (*F_o*² + 2*F_c*²)/3

(Δσ)_{max} = 0.005

Δρ_{max} = 0.59 e Å⁻³

Δρ_{min} = -0.40 e Å⁻³

Primary atom site location: structure-invariant direct methods Extinction correction: none

Special details

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

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.5000	-0.02872 (10)	0.2500	0.0174 (3)
S2	0.46838 (4)	0.23246 (7)	0.30370 (8)	0.0183 (2)
N1	0.32997 (13)	0.1448 (3)	0.5839 (3)	0.0188 (6)
O1	0.39897 (11)	0.2266 (2)	0.4329 (2)	0.0222 (5)
C1	0.39538 (15)	0.1118 (3)	0.4513 (3)	0.0172 (7)
C2	0.42747 (15)	0.0229 (3)	0.3960 (3)	0.0161 (7)
C3	0.42230 (15)	-0.1102 (3)	0.4154 (3)	0.0192 (7)
H3	0.4425	-0.1664	0.3776	0.023*
C4	0.38870 (15)	-0.1536 (3)	0.4873 (3)	0.0190 (7)
H4	0.3863	-0.2395	0.4988	0.023*
C5	0.35623 (14)	-0.0699 (3)	0.5473 (3)	0.0164 (7)
C6	0.32260 (15)	-0.1123 (3)	0.6273 (3)	0.0209 (7)
H6	0.3204	-0.1973	0.6437	0.025*
C7	0.29310 (15)	-0.0268 (3)	0.6809 (3)	0.0203 (7)
H7	0.2703	-0.0539	0.7329	0.024*
C8	0.29742 (15)	0.1021 (3)	0.6570 (3)	0.0201 (7)
C9	0.35899 (14)	0.0610 (3)	0.5305 (3)	0.0162 (7)
C10	0.46249 (14)	0.0732 (3)	0.3239 (3)	0.0160 (6)
C11	0.26353 (17)	0.1970 (3)	0.7105 (4)	0.0282 (8)
H11A	0.2813	0.2779	0.7113	0.042*
H11B	0.2633	0.1734	0.7937	0.042*
H11C	0.2243	0.2004	0.6606	0.042*
C12	0.38385 (16)	0.4303 (3)	0.6259 (3)	0.0219 (7)
H12	0.3788	0.3427	0.5991	0.026*
C11	0.32240 (4)	0.51737 (9)	0.54728 (9)	0.0323 (3)
C12	0.39044 (5)	0.43802 (10)	0.78724 (8)	0.0365 (3)
C13	0.44742 (4)	0.49030 (9)	0.59141 (8)	0.0295 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0206 (6)	0.0128 (5)	0.0219 (6)	0.000	0.0114 (5)	0.000
S2	0.0218 (4)	0.0134 (4)	0.0231 (4)	0.0000 (3)	0.0118 (3)	0.0000 (3)
N1	0.0201 (15)	0.0185 (14)	0.0187 (14)	-0.0012 (12)	0.0069 (12)	-0.0015 (11)
O1	0.0299 (14)	0.0155 (11)	0.0253 (13)	-0.0025 (10)	0.0144 (11)	-0.0007 (10)

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C1	0.0178 (17)	0.0157 (15)	0.0173 (16)	0.0004 (13)	0.0028 (13)	0.0009 (12)
C2	0.0141 (16)	0.0183 (15)	0.0164 (15)	-0.0018 (13)	0.0048 (13)	-0.0015 (12)
C3	0.0204 (18)	0.0174 (16)	0.0217 (17)	-0.0004 (13)	0.0089 (14)	-0.0005 (13)
C4	0.0183 (17)	0.0142 (15)	0.0254 (17)	-0.0005 (13)	0.0074 (14)	0.0003 (13)
C5	0.0148 (16)	0.0175 (15)	0.0157 (15)	-0.0020 (13)	0.0015 (13)	0.0009 (12)
C6	0.0211 (18)	0.0183 (16)	0.0234 (17)	-0.0016 (13)	0.0060 (14)	0.0026 (14)
C7	0.0160 (17)	0.0256 (17)	0.0208 (17)	-0.0018 (14)	0.0076 (14)	0.0030 (14)
C8	0.0176 (17)	0.0227 (17)	0.0204 (16)	0.0004 (14)	0.0056 (14)	-0.0026 (14)
C9	0.0145 (16)	0.0177 (15)	0.0162 (15)	-0.0003 (13)	0.0032 (13)	-0.0010 (13)
C10	0.0155 (16)	0.0149 (15)	0.0178 (15)	-0.0008 (13)	0.0046 (13)	-0.0009 (12)
C11	0.031 (2)	0.0263 (18)	0.034 (2)	0.0012 (16)	0.0195 (17)	-0.0018 (16)
C12	0.029 (2)	0.0193 (17)	0.0181 (16)	-0.0035 (14)	0.0078 (14)	-0.0009 (13)
Cl1	0.0272 (5)	0.0319 (5)	0.0356 (5)	0.0022 (4)	0.0036 (4)	0.0045 (4)
Cl2	0.0503 (7)	0.0422 (6)	0.0191 (4)	-0.0079 (5)	0.0125 (4)	0.0023 (4)
Cl3	0.0260 (5)	0.0393 (5)	0.0240 (5)	-0.0087 (4)	0.0075 (4)	-0.0044 (4)

Geometric parameters (Å, °)

S1—C10 ⁱ	1.735 (3)	C5—C6	1.406 (5)
S1—C10	1.735 (3)	C5—C9	1.414 (5)
S2—C10	1.725 (3)	C6—C7	1.371 (5)
S2—S2 ⁱ	2.1338 (16)	C6—H6	0.9300
N1—C8	1.331 (4)	C7—C8	1.410 (5)
N1—C9	1.351 (4)	C7—H7	0.9300
O1—C1	1.248 (4)	C8—C11	1.503 (5)
C1—C2	1.445 (5)	C11—H11A	0.9600
C1—C9	1.479 (5)	C11—H11B	0.9600
C2—C10	1.395 (5)	C11—H11C	0.9600
C2—C3	1.447 (4)	C12—Cl2	1.763 (3)
C3—C4	1.342 (5)	C12—Cl3	1.765 (4)
C3—H3	0.9300	C12—Cl1	1.769 (4)
C4—C5	1.445 (5)	C12—H12	0.9800
C4—H4	0.9300		
C10 ⁱ —S1—C10	102.3 (2)	C8—C7—H7	120.0
C10—S2—S2 ⁱ	99.41 (11)	N1—C8—C7	121.9 (3)
C8—N1—C9	118.4 (3)	N1—C8—C11	117.2 (3)
O1—C1—C2	120.8 (3)	C7—C8—C11	120.8 (3)
O1—C1—C9	122.0 (3)	N1—C9—C5	123.5 (3)
C2—C1—C9	117.2 (3)	N1—C9—C1	117.0 (3)
C10—C2—C1	116.2 (3)	C5—C9—C1	119.6 (3)
C10—C2—C3	123.2 (3)	C2—C10—S2	122.2 (2)
C1—C2—C3	120.6 (3)	C2—C10—S1	118.5 (2)
C4—C3—C2	120.8 (3)	S2—C10—S1	119.27 (19)
C4—C3—H3	119.6	C8—C11—H11A	109.5
C2—C3—H3	119.6	C8—C11—H11B	109.5
C3—C4—C5	121.6 (3)	H11A—C11—H11B	109.5
C3—C4—H4	119.2	C8—C11—H11C	109.5
C5—C4—H4	119.2	H11A—C11—H11C	109.5

C6—C5—C9	116.9 (3)	H11B—C11—H11C	109.5
C6—C5—C4	122.8 (3)	C12—C12—C13	109.62 (19)
C9—C5—C4	120.2 (3)	C12—C12—C11	109.6 (2)
C7—C6—C5	119.3 (3)	C13—C12—C11	110.34 (19)
C7—C6—H6	120.3	C12—C12—H12	109.1
C5—C6—H6	120.3	C13—C12—H12	109.1
C6—C7—C8	119.9 (3)	C11—C12—H12	109.1
C6—C7—H7	120.0		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D—H\cdotsA</i>	<i>D—H</i>	<i>H\cdotsA</i>	<i>D\cdotsA</i>	<i>D—H\cdotsA</i>
C3—H3 \cdots S1	0.93	2.64	3.032 (3)	106
C12—H12 \cdots O1	0.98	2.37	3.136 (4)	135
C12—H12 \cdots N1	0.98	2.40	3.294 (4)	152

Main π – π interactions in (I) ($\text{\AA}, ^\circ$)

DA is dihedral angle between the planes, DCC is the length of the CC vector (centroid to centroid), τ is the angle(s) subtended by the plane normal(s) to CC. Cg1 is the centroid of ring S1-C10-S2-S2ⁱ-C10ⁱ, Cg2 of ring C1-C5/C9.

Group 1	Group 2	DA	DCC	τ
Cg1	Cg2 ⁱ	3.62	3.650 (2)	16.31
Cg1	Cg2 ⁱⁱ	3.62	3.650 (2)	16.31

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

Fig. 1

