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4,4′,6,6′-Tetramethyl-2,2′-(ethylenedithio)dipyrimidine

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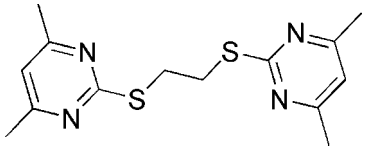
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.043; wR factor = 0.144; data-to-parameter ratio = 18.2.

The unit cell of the crystal structure of the title compound, $C_{14}H_{18}N_4S_2$, contains two crystallographically independent molecules, each located on an inversion center. The centroid-to-centroid separation of 3.478 (2) Å indicates the existence of π–π stacking between parallel pyrimidine rings of adjacent molecules.

Related literature

For related literature, see: Nishihara *et al.* (1989); Roberto *et al.* (2000).



Experimental

Crystal data

$C_{14}H_{18}N_4S_2$
M_r = 306.44
Triclinic, $P\overline{1}$
a = 8.487 (5) Å
b = 9.167 (5) Å
c = 10.557 (5) Å
α = 85.282 (5)°
β = 83.264 (5)°
γ = 89.711 (5)°
V = 812.9 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 293 (2) K
0.46 × 0.34 × 0.31 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.866, T_{max} = 0.907
11764 measured reflections
3721 independent reflections
3008 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.144
S = 1.38
3721 reflections
204 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2299).

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supplementary materials

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4,4',6,6'-Tetramethyl-2,2'-(ethylenedithio)dipyrimidine

G.-H. Wu, X.-M. Wu, J.-P. Zhang and T.-B. Liu

Comment

Previous studies have shown that heterocycle-based aromatic systems with conjugated multi-branched structure possess potential applications in optical image processing, all-optical switching, and integrated optical devices (Nishihara *et al.*, 1989; Roberto *et al.*, 2000). Therefore we pay our attention to the pyrimidine system, which has well known reactivity in the pyrimidine ring (positions 2, 4 and 6) and can easily be modified to conjugated multi-branched structures. As part of our ongoing investigation on pyrimidine derivatives, the title compound has been prepared and its crystal structure is presented here.

There are two crystallographically independent molecules, located on individual inversion center (Fig. 1). Bond lengths and angles in the two molecules are similar. The two pyrimidine rings are planar and parallel. The crystal packing (Fig. 2) is mainly stabilized by π–π stacking, the centroid-to-centroid separation between parallel N3-pyrimidine and N3^{i}-pyrimidine rings being of 3.478 (2) Å [symmetry code: (i) 1 − *x*, −*y*, 2 − *z*].

Experimental

A solution of 1,2-dibromoethane (0.94 g, 5 mmol) in ethanol (10 ml) was slowly dropped into a refluxing solution of 2-thiol-4,6-dimethylpyrimidine (1.40 g, 10 mmol) and NaOH (0.4 g, 10 mmol) in ethanol (20 ml). The reaction mixture was refluxed for 3 h and then cooled to room temperature. The white powder of title compound was filtered and washed thoroughly with water and then air dried (yield 55%). Single crystals suitable for X-ray analysis were obtained by slow evaporation from a dichloromethane/2-propanol (3:1) solution.

Refinement

For one of independent molecules, the ethylenedithio moiety was disordered over two sites. The occupancies were refined and converged to 0.502 (10):0.498 (10). H atoms were positioned geometrically with C—H = 0.93 (aromatic), 0.97 (methylene) and 0.96 Å (methyl), and refined in riding mode with U_{iso}(H) = xU_{eq}(C), where x = 1.5 for methyl H and x = 1.2 for others.

Figures

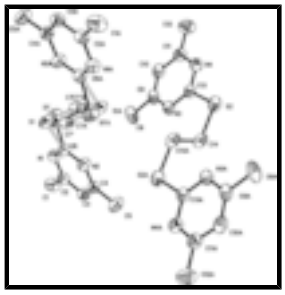

Fig. 1. The molecular structure of the title compound showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

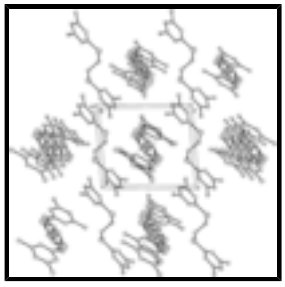

Fig. 2. Packing diagram of of the title compound viewed along the *a* axis. Hydrogen atoms are omitted for clarity.

4,4',6,6'-Tetramethyl-2,2'-(ethylenedithio)dipyrimidine

Crystal data

$C_{14}H_{18}N_4S_2$	$Z = 2$
$M_r = 306.44$	$F_{000} = 324$
Triclinic, $P\bar{1}$	$D_x = 1.252$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
$a = 8.487$ (5) Å	Cell parameters from 5112 reflections
$b = 9.167$ (5) Å	$\theta = 1.9$–27.5°
$c = 10.557$ (5) Å	$\mu = 0.32$ mm^{-1}
$\alpha = 85.282$ (5)°	$T = 293$ (2) K
$\beta = 83.264$ (5)°	Block, orange-yellow
$\gamma = 89.711$ (5)°	0.46 × 0.34 × 0.31 mm
$V = 812.9$ (8) Å^3	

Data collection

Bruker APEXII CCD area-detector diffractometer	3721 independent reflections
Radiation source: fine-focus sealed tube	3008 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.020$
$T = 293$(2) K	$\theta_{max} = 27.5^\circ$
φ and ω scans	$\theta_{min} = 1.9^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -11 \rightarrow 11$
$T_{min} = 0.866$, $T_{max} = 0.907$	$k = -11 \rightarrow 11$

11764 measured reflections

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.144$

$S = 1.38$

3721 reflections

204 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0741P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.22$ e Å^{-3}

$\Delta\rho_{min} = -0.24$ e Å^{-3}

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	−0.1753 (2)	0.1379 (2)	0.4757 (2)	0.0806 (6)	
H1A	−0.1925	0.1757	0.3909	0.121*	
H1B	−0.2735	0.1379	0.5309	0.121*	
H1C	−0.1358	0.0397	0.4734	0.121*	
C2	−0.05600 (17)	0.23267 (15)	0.52551 (16)	0.0548 (4)	
C3	−0.08802 (18)	0.29944 (17)	0.63776 (15)	0.0570 (4)	
H3	−0.1856	0.2861	0.6875	0.068*	
C4	0.02799 (18)	0.38698 (17)	0.67507 (15)	0.0548 (4)	
C5	0.0014 (2)	0.4651 (2)	0.79489 (18)	0.0830 (6)	
H5A	0.0663	0.4221	0.8564	0.125*	
H5B	−0.1083	0.4567	0.8295	0.125*	
H5C	0.0290	0.5666	0.7755	0.125*	
C6	0.18869 (18)	0.33423 (17)	0.49854 (14)	0.0544 (4)	
C7	0.5087 (5)	0.4183 (5)	0.5078 (5)	0.0581 (14)	0.498 (10)
H7A	0.4760	0.3784	0.5948	0.070*	0.498 (10)
H7B	0.6158	0.3871	0.4804	0.070*	0.498 (10)
C8	0.3687 (3)	0.0925 (2)	0.7483 (2)	0.0881 (6)	

H8A	0.3110	0.0028	0.7725	0.132*	
H8B	0.4025	0.0993	0.6580	0.132*	
H8C	0.3014	0.1739	0.7686	0.132*	
C9	0.5109 (2)	0.09497 (17)	0.81995 (15)	0.0595 (4)	
C10	0.6268 (2)	−0.00835 (17)	0.80949 (16)	0.0642 (4)	
H10	0.6211	−0.0824	0.7550	0.077*	
C11	0.7522 (2)	−0.00184 (18)	0.88059 (16)	0.0630 (4)	
C12	0.8825 (3)	−0.1125 (3)	0.8756 (3)	0.0996 (7)	
H12A	0.9827	−0.0639	0.8738	0.149*	
H12B	0.8822	−0.1638	0.7999	0.149*	
H12C	0.8661	−0.1810	0.9498	0.149*	
C13	0.64045 (18)	0.19983 (16)	0.96409 (14)	0.0519 (3)	
C14	0.4877 (2)	0.44566 (18)	1.05891 (16)	0.0666 (4)	
H14A	0.3960	0.3848	1.0533	0.080*	
H14B	0.4659	0.4989	1.1347	0.080*	
C7'	0.4535 (4)	0.5207 (6)	0.4450 (4)	0.0563 (14)	0.502 (10)
H7C	0.5195	0.5677	0.3719	0.068*	0.502 (10)
H7D	0.3642	0.5830	0.4692	0.068*	0.502 (10)
N1	0.08528 (15)	0.24921 (13)	0.45450 (12)	0.0554 (3)	
N2	0.16878 (15)	0.40563 (15)	0.60426 (12)	0.0580 (3)	
N3	0.51650 (15)	0.20336 (14)	0.89806 (12)	0.0573 (3)	
N4	0.75976 (15)	0.10482 (15)	0.95989 (13)	0.0609 (4)	
S1	0.3561 (4)	0.3698 (6)	0.3876 (3)	0.0653 (6)	0.498 (10)
S2	0.65828 (6)	0.33032 (5)	1.07490 (4)	0.06776 (18)	
S1'	0.3855 (4)	0.3241 (4)	0.4131 (4)	0.0627 (6)	0.502 (10)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0612 (11)	0.0723 (11)	0.1141 (16)	−0.0139 (9)	−0.0200 (10)	−0.0279 (11)
C2	0.0493 (8)	0.0444 (7)	0.0728 (10)	−0.0037 (6)	−0.0167 (7)	−0.0038 (7)
C3	0.0460 (8)	0.0578 (8)	0.0659 (9)	−0.0067 (6)	−0.0029 (7)	−0.0012 (7)
C4	0.0517 (8)	0.0603 (8)	0.0524 (8)	−0.0060 (6)	−0.0031 (6)	−0.0077 (7)
C5	0.0730 (12)	0.1109 (16)	0.0656 (11)	−0.0186 (11)	0.0084 (9)	−0.0321 (10)
C6	0.0524 (8)	0.0573 (8)	0.0541 (8)	−0.0100 (6)	−0.0029 (6)	−0.0113 (6)
C7	0.0451 (18)	0.054 (2)	0.074 (3)	−0.0017 (15)	−0.0004 (17)	−0.010 (2)
C8	0.0991 (15)	0.0875 (13)	0.0861 (13)	−0.0213 (11)	−0.0510 (12)	0.0004 (10)
C9	0.0734 (11)	0.0564 (8)	0.0505 (8)	−0.0190 (7)	−0.0179 (7)	0.0004 (7)
C10	0.0821 (12)	0.0565 (9)	0.0565 (8)	−0.0137 (8)	−0.0108 (8)	−0.0142 (7)
C11	0.0658 (10)	0.0618 (9)	0.0631 (9)	−0.0048 (8)	−0.0072 (8)	−0.0164 (7)
C12	0.0869 (15)	0.0971 (16)	0.122 (2)	0.0188 (12)	−0.0169 (14)	−0.0479 (14)
C13	0.0581 (9)	0.0514 (8)	0.0469 (7)	−0.0114 (6)	−0.0064 (6)	−0.0069 (6)
C14	0.0799 (11)	0.0591 (9)	0.0580 (9)	−0.0045 (8)	0.0090 (8)	−0.0122 (7)
C7'	0.0485 (18)	0.061 (3)	0.057 (2)	−0.0077 (17)	0.0011 (15)	−0.0031 (19)
N1	0.0557 (7)	0.0502 (7)	0.0626 (7)	−0.0053 (5)	−0.0103 (6)	−0.0135 (5)
N2	0.0523 (7)	0.0691 (8)	0.0531 (7)	−0.0154 (6)	0.0003 (6)	−0.0167 (6)
N3	0.0622 (8)	0.0553 (7)	0.0559 (7)	−0.0086 (6)	−0.0139 (6)	−0.0036 (6)
N4	0.0571 (8)	0.0652 (8)	0.0633 (8)	−0.0058 (6)	−0.0108 (6)	−0.0171 (6)

S1	0.0560 (10)	0.0808 (15)	0.0580 (8)	−0.0124 (9)	0.0088 (6)	−0.0198 (9)
S2	0.0806 (3)	0.0653 (3)	0.0617 (3)	−0.0084 (2)	−0.0146 (2)	−0.0215 (2)
S1'	0.0550 (9)	0.0644 (11)	0.0685 (11)	−0.0105 (7)	0.0076 (7)	−0.0259 (9)

Geometric parameters (Å, °)

C1—C2	1.505 (2)	C8—H8B	0.9600
C1—H1A	0.9600	C8—H8C	0.9600
C1—H1B	0.9600	C9—N3	1.347 (2)
C1—H1C	0.9600	C9—C10	1.363 (2)
C2—N1	1.340 (2)	C10—C11	1.377 (2)
C2—C3	1.377 (2)	C10—H10	0.9300
C3—C4	1.385 (2)	C11—N4	1.3450 (19)
C3—H3	0.9300	C11—C12	1.496 (3)
C4—N2	1.337 (2)	C12—H12A	0.9600
C4—C5	1.498 (2)	C12—H12B	0.9600
C5—H5A	0.9600	C12—H12C	0.9600
C5—H5B	0.9600	C13—N3	1.3272 (18)
C5—H5C	0.9600	C13—N4	1.331 (2)
C6—N1	1.3253 (19)	C13—S2	1.7595 (16)
C6—N2	1.3331 (19)	C14—C14^{ii}	1.523 (3)
C6—S1	1.746 (3)	C14—S2	1.804 (2)
C6—S1'	1.808 (3)	C14—H14A	0.9700
C7—C7^{i}	1.501 (9)	C14—H14B	0.9700
C7—S1	1.993 (6)	C7'—C7'^{i}	1.503 (9)
C7—H7A	0.9700	C7'—S1'	1.962 (6)
C7—H7B	0.9700	C7'—H7C	0.9700
C8—C9	1.499 (2)	C7'—H7D	0.9700
C8—H8A	0.9600		
C2—C1—H1A	109.5	N3—C9—C10	121.50 (14)
C2—C1—H1B	109.5	N3—C9—C8	116.28 (16)
H1A—C1—H1B	109.5	C10—C9—C8	122.20 (16)
C2—C1—H1C	109.5	C9—C10—C11	119.23 (15)
H1A—C1—H1C	109.5	C9—C10—H10	120.4
H1B—C1—H1C	109.5	C11—C10—H10	120.4
N1—C2—C3	121.02 (13)	N4—C11—C10	120.31 (15)
N1—C2—C1	116.35 (15)	N4—C11—C12	117.42 (16)
C3—C2—C1	122.63 (16)	C10—C11—C12	122.26 (16)
C2—C3—C4	118.66 (15)	C11—C12—H12A	109.5
C2—C3—H3	120.7	C11—C12—H12B	109.5
C4—C3—H3	120.7	H12A—C12—H12B	109.5
N2—C4—C3	120.86 (15)	C11—C12—H12C	109.5
N2—C4—C5	117.29 (14)	H12A—C12—H12C	109.5
C3—C4—C5	121.85 (15)	H12B—C12—H12C	109.5
C4—C5—H5A	109.5	N3—C13—N4	127.89 (14)
C4—C5—H5B	109.5	N3—C13—S2	119.91 (12)
H5A—C5—H5B	109.5	N4—C13—S2	112.20 (11)
C4—C5—H5C	109.5	C14^{ii}—C14—S2	112.22 (17)

H5A—C5—H5C	109.5	$C14^{ii}$—C14—H14A	109.2
H5B—C5—H5C	109.5	S2—C14—H14A	109.2
N1—C6—N2	127.90 (14)	$C14^{ii}$—C14—H14B	109.2
N1—C6—S1	111.75 (14)	S2—C14—H14B	109.2
N2—C6—S1	119.71 (14)	H14A—C14—H14B	107.9
N1—C6—S1'	112.50 (14)	$C7^{i}$—C7'—S1'	98.6 (4)
N2—C6—S1'	118.89 (14)	$C7^{i}$—C7'—H7C	112.1
$C7^{i}$—C7—S1	97.3 (4)	S1'—C7'—H7C	112.1
$C7^{i}$—C7—H7A	112.3	$C7^{i}$—C7'—H7D	112.1
S1—C7—H7A	112.3	S1'—C7'—H7D	112.1
$C7^{i}$—C7—H7B	112.3	H7C—C7'—H7D	109.7
S1—C7—H7B	112.3	C6—N1—C2	115.82 (14)
H7A—C7—H7B	109.9	C6—N2—C4	115.73 (13)
C9—C8—H8A	109.5	C13—N3—C9	115.11 (13)
C9—C8—H8B	109.5	C13—N4—C11	115.95 (13)
H8A—C8—H8B	109.5	C6—S1—C7	98.73 (17)
C9—C8—H8C	109.5	C13—S2—C14	103.18 (8)
H8A—C8—H8C	109.5	C6—S1'—C7'	96.10 (16)
H8B—C8—H8C	109.5		
N1—C2—C3—C4	1.3 (2)	S2—C13—N3—C9	−177.29 (10)
C1—C2—C3—C4	−178.81 (16)	C10—C9—N3—C13	−1.0 (2)
C2—C3—C4—N2	−0.5 (2)	C8—C9—N3—C13	177.51 (14)
C2—C3—C4—C5	179.09 (15)	N3—C13—N4—C11	−1.2 (2)
N3—C9—C10—C11	0.1 (3)	S2—C13—N4—C11	177.79 (11)
C8—C9—C10—C11	−178.30 (17)	C10—C11—N4—C13	0.1 (2)
C9—C10—C11—N4	0.3 (3)	C12—C11—N4—C13	−178.68 (18)
C9—C10—C11—C12	179.08 (19)	N1—C6—S1—C7	−157.0 (2)
N2—C6—N1—C2	−0.4 (2)	N2—C6—S1—C7	31.4 (4)
S1—C6—N1—C2	−171.1 (2)	S1'—C6—S1—C7	−61.0 (5)
S1'—C6—N1—C2	169.7 (2)	$C7^{i}$—C7—S1—C6	−96.1 (3)
C3—C2—N1—C6	−0.8 (2)	N3—C13—S2—C14	−2.25 (14)
C1—C2—N1—C6	179.23 (13)	N4—C13—S2—C14	178.69 (12)
N1—C6—N2—C4	1.1 (2)	$C14^{ii}$—C14—S2—C13	−78.53 (18)
S1—C6—N2—C4	171.2 (2)	N1—C6—S1'—C7'	153.0 (2)
S1'—C6—N2—C4	−168.4 (2)	N2—C6—S1'—C7'	−35.9 (4)
C3—C4—N2—C6	−0.6 (2)	S1—C6—S1'—C7'	61.7 (5)
C5—C4—N2—C6	179.79 (15)	$C7^{i}$—C7'—S1'—C6	99.1 (3)
N4—C13—N3—C9	1.6 (2)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*+2.

Fig. 1

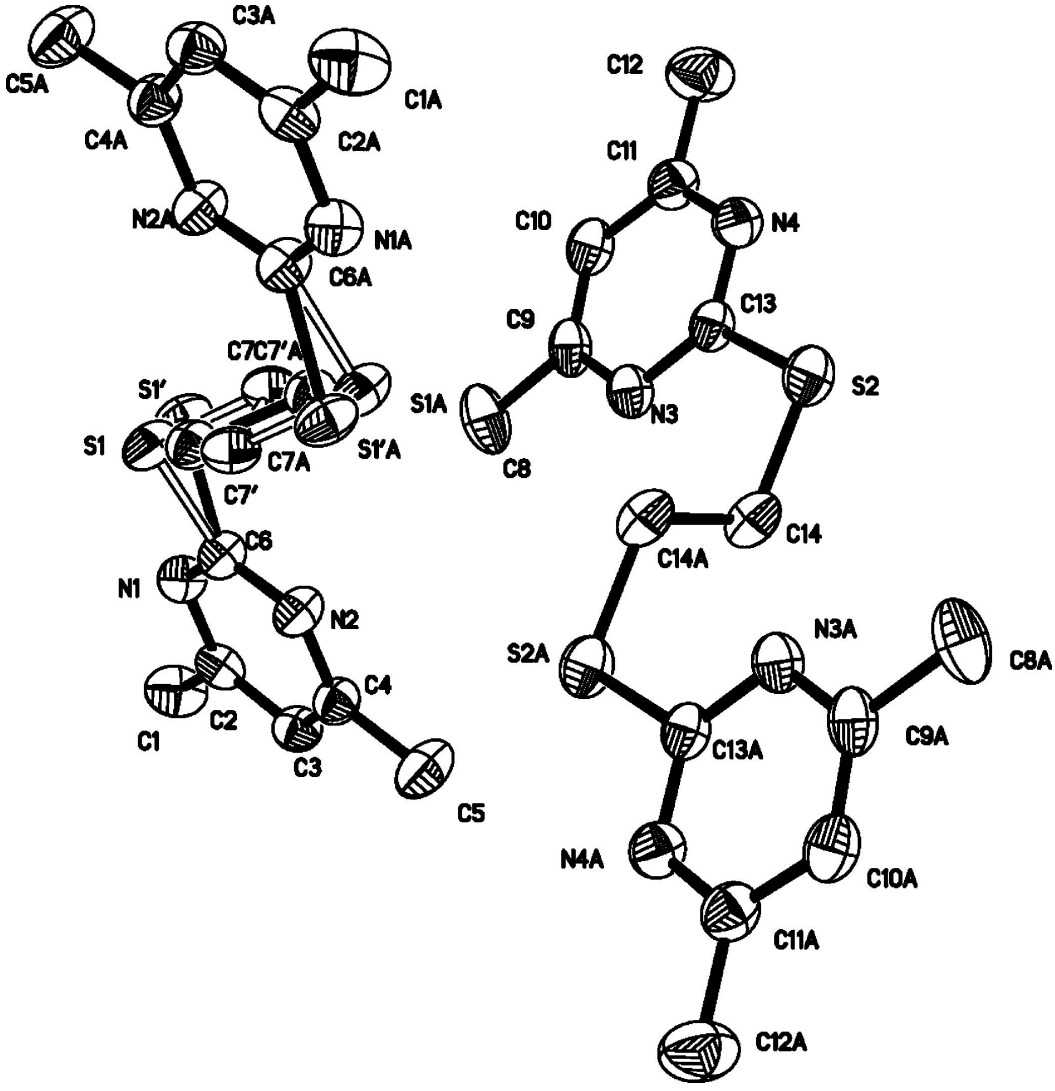
C3A
C5A
C1A
C4A
C2A
N2A
N1A
C6A
C7C7'A
S1'
S1A
S1
C7A
S1'A
C7'
C6
N1
N2
C4
C2
C1
C3
C5
C12
C11
C10
N4
C13
C9
S2
N3
C8
C14
C14A
N3A
S2A
C8A
C13A
C9A
N4A
C10A
C11A
C12A

Fig. 2