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N,*N*′-Diisopentyldithiooxamide

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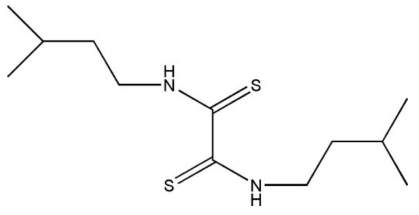
Key indicators: single-crystal X-ray study; T = 571 K; mean σ(C–C) = 0.003 Å; R factor = 0.034; wR factor = 0.098; data-to-parameter ratio = 20.6.

In the crystal structure of the centrosymmetric dithiooxamide title compound, $C_{12}H_{24}N_2S_2$, one half-molecule is present in the asymmetric unit and the entire molecule is generated by inversion. As is usual for secondary dithiooxamides, the title compound shows the *trans*-planar conformation. Crystal packing is mainly supported by intermolecular N—H⋯S and C—H⋯S interactions developing flat ribbon-like one-dimensional arrays. These are stacked vertically through π–π interactions of the core frames [regular mean plane distances of 3.659 (1) Å], and the three-dimensional packing is completed by nonpolar interactions involving the alkyl chains.

Related literature

For related literature, see: Aversa *et al.* (1997, 2000); Bermejo *et al.* (1998); Cremer & Pople (1975); Desseyn *et al.* (1978); Hurd *et al.* (1961); Jean (1994); Lanza *et al.* (2000, 2002, 2003, 2005); Perec *et al.* (1995); Shimanouchi & Sasada (1979); Simonov *et al.* (2003); Veit *et al.* (1984); Ye *et al.* (1991).



Experimental

Crystal data

$C_{12}H_{24}N_2S_2$
M_r = 260.45
Triclinic, $P\bar{1}$
a = 4.7658 (9) Å
b = 6.0323 (9) Å
c = 14.470 (2) Å
α = 83.082 (14)°
β = 85.919 (15)°
γ = 70.427 (15)°
V = 388.90 (11) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 571 (2) K
0.58 × 0.44 × 0.24 mm

Data collection

Bruker *P*4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.825, T_{max} = 0.924
2093 measured reflections
1523 independent reflections
1344 reflections with $I > 2\sigma(I)$
R_{int} = 0.011
3 standard reflections every 197 reflections intensity decay: 2%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.098
S = 1.12
1523 reflections
74 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Table 1
Selected bond lengths (Å).

S1—C1	1.6606 (15)	N1—C2	1.454 (2)
N1—C1	1.3165 (19)	C1—C1^{i}	1.522 (3)

Symmetry code: (i) $-x+1, -y+1, -z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯S1^{i}	0.86	2.45	2.9452 (15)	118
N1—H1⋯S1^{ii}	0.86	2.80	3.4251 (14)	131
C2—H2B⋯S1^{ii}	0.97	2.99	3.4991 (18)	114

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

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XPREP* (Bruker, 1997); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1997); software used to prepare material for publication: *PARST95* (Nardelli, 1995) and *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HJ3049).

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supplementary materials

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N,*N*'-Diisopentyldithiooxamide

G. Bruno, A. Rotondo, F. Nicoló and S. Lanza

Comment

Secondary dithioxamides behave as binucleating ligands both in N,*S*–N,*S* (Veit *et al.*, 1984; Ye *et al.*, 1991; Lanza *et al.* 2002) and in N,*N*–S,*S* modes (Lanza *et al.*, 2000; 2003; 2005) (Scheme 1). It has been already observed (Lanza *et al.*, 2005) that in the trimetallic complexes $[Pt\{\{\mu\text{-}S_2C_2(NR)_2\}ML_n\}_2]$ ($\mu\text{-}S_2C_2(NR)_2$ = bridging dianionic dithioxamidate; ML_n^+= positively charged metal fragment) there is an electron removal from platinum to ML_n^+ *via* the π^* system in the N—C—S fragments (Lanza *et al.* 2005). The possibility of a π donation from the bridged dithioxamide to the platinum d orbitals has been ruled out, since this latter circumstance would require a C—C double bond connecting the two N—C—S frames. In order to asses factors affecting electronic transmission between metals in polymetallic chains through binucleating dithioxamides, we think it is important to gain as much structural information as possible about free and coordinated $H_2S_2C_2(NR)_2$ ligands

The asymmetric unit of (I) contains one half of the symmetric molecule with the other half generated by inversion (Fig. 1). The thioamide moiety is planar [maximum deviation from the mean plane for the C1 = 0.001 (1) Å]; the *trans* conformation is also stabilized by the intramolecular interaction N—H···S [N1—H1 = 0.860 (1), N1···S1^i = 2.945 (1) Å, N1—H1···S1^i = 117.6 (1)°; symmetry code (i) −*x* + 1, −*y* + 1, −*z*], moreover the first C atom of the N-attached alkyl chain keeps the planarity of the core atoms [maximum deviation of C2 = 0.005 (2) Å]. On the other hand the features of the sp^3 hybridized C atoms mean that the side aliphatic chains are above and below with respect to the core planar fragment. The thioamide geometrical parameters in the table are in accord with those found for similar crystal structures (Shimanouchi & Sasada, 1979; Bermejo *et al.*, 1998; Perec *et al.*, 1995; Jean 1994; Simonov *et al.* 2003).

The crystal lattice is mainly supported by intermolecular N—H···S interactions [N1—H1 = 0.860 (1), N1···S1^{ii} = 3.425 (2) Å, N1—H1···S1^{ii} = 131.3 (1)°; symmetry code (ii) *x*, *y* + 1, *z*] together with a much weaker C—H···S hydrogen bond [C2—H2B = 0.970 (2), C1···S1^{ii} = 3.499 (2) Å, C2—H2B···S1^{ii} = 114.1 (1)°]. The interaction N—H···S doubled by the crystallographic inversion centre leads to the "chain of rings" $C(3)R_2^2(10)$ motif (Bernstein *et al.*, 1995). The resulting one-dimensional-array of molecules along the b crystallographic axis looks like a planar strand because of the directional self-recognition (Fig. 2). The thioamidic group also develops vertical π-π interactions [distance from the mean thioxamidic planes 3.6595 (5) Å; symmetry code for the π stacked equivalent is *x* + 1, *y*, *z*] generating a ladder like disposition of the planar strands running along the a crystallographic axis (Fig. 3). The non-polar nature of the alkylic chain means that very weak interactions complete the third dimension of the crystal packing. Compounds with similar structure can be regarded as forerunners of metallomesogens; actually mesophases are observed when the *R* groups are aryl substituents bearing long hydrocarbon chains (Aversa *et al.*, 2000; 1997).

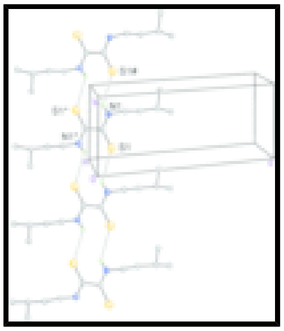
Experimental

The title compound I was synthesized according to Hurd *et al.* (1961). crystals were obtained by recrystallization from a chloroform-petrol ether (1:1) solution.

Refinement

Hydrogen atoms were localized from the difference Fourier map and idealized by the well known "riding-model technique" with distances to the parent atoms of of 0.96 to 0.98 Å. The best refinement was obtained with the psi-scan (North *et al.*, 1968) absorption correction performed by *XSCANS* (Siemens, 1989).

Figures



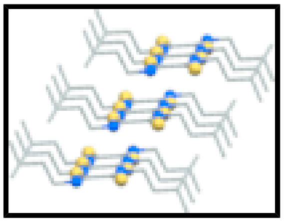
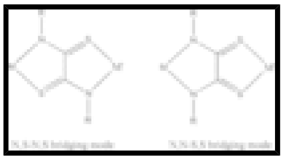


Fig. 1. The molecule of (I), showing the atom numbering scheme. Displacement ellipsoids are drawn at 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Fig. 2. Part of the crystal structure of (I), showing the formation of the chain of rings C(3)R_2^2(10) along [010]. Atoms marked with an asterisk (*) or an hash (#) are at the symmetry positions ($-x + 1$, $-y + 1$, $-z$) and (x, $y + 1$, z), respectively. For the sake of clarity all H atoms uninvolved in the evidenced interactions are omitted.

Fig. 3. Ladder-like stacking of one-dimensional-arrays of (I). Strands are aligned along the [100] direction.



N,*N*'-Diisopentyldithiooxamide

Crystal data

$C_{12}H_{24}N_2S_2$
M_r = 260.45
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 4.7658 (9) Å
b = 6.0323 (9) Å
c = 14.470 (2) Å
α = 83.082 (14)°

Z = 1
F_{000} = 142
D_x = 1.112 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 66 reflections
θ = 4.8–22.5°
μ = 0.32 mm^{-1}
T = 571 (2) K

$\beta = 85.919\ (15)°$
$\gamma = 70.427\ (15)°$
$V = 388.90\ (11)$ Å^3

Irregular, yellow
0.58 × 0.44 × 0.24 mm

Data collection

Bruker P4 diffractometer
2θ/ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.825$, $T_{\max} = 0.924$
2093 measured reflections
1523 independent reflections
1344 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.011$

$\theta_{\max} = 26.0°$
$\theta_{\min} = 2.8°$
$h = -1 \rightarrow 5$
$k = -7 \rightarrow 7$
$l = -17 \rightarrow 17$
3 standard reflections
every 197 reflections
intensity decay: 2%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.098$
$S = 1.12$
1523 reflections
74 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 0.0753P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.30375 (11)	0.27375 (7)	0.08976 (3)	0.05646 (19)
N1	0.2847 (3)	0.7182 (2)	0.07141 (9)	0.0431 (3)
H1	0.3425	0.8287	0.042	0.052*
C1	0.3922 (3)	0.5069 (2)	0.04182 (10)	0.0384 (3)
C2	0.0759 (4)	0.7793 (3)	0.15000 (11)	0.0475 (4)
H2A	−0.0553	0.6852	0.1543	0.057*
H2B	−0.0457	0.9446	0.1398	0.057*
C3	0.2347 (4)	0.7371 (3)	0.24076 (12)	0.0534 (4)
H3A	0.3617	0.8346	0.2365	0.064*

H3B	0.3618	0.5731	0.2493	0.064*
C4	0.0254 (5)	0.7911 (4)	0.32571 (13)	0.0641 (5)
H4	−0.117	0.706	0.325	0.077*
C5	−0.1497 (7)	1.0529 (5)	0.32366 (19)	0.0993 (9)
H5A	−0.256	1.1057	0.2669	0.149*
H5B	−0.0152	1.1396	0.327	0.149*
H5C	−0.2888	1.0791	0.3758	0.149*
C6	0.1984 (7)	0.7021 (6)	0.41444 (15)	0.1009 (9)
H6A	0.3081	0.5365	0.4142	0.151*
H6B	0.0623	0.7259	0.4674	0.151*
H6C	0.3343	0.7875	0.4179	0.151*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0758 (3)	0.0383 (2)	0.0581 (3)	−0.0242 (2)	0.0082 (2)	−0.00594 (18)
N1	0.0514 (8)	0.0345 (6)	0.0446 (7)	−0.0147 (5)	−0.0004 (6)	−0.0075 (5)
C1	0.0432 (8)	0.0345 (7)	0.0376 (7)	−0.0117 (6)	−0.0091 (6)	−0.0036 (6)
C2	0.0481 (9)	0.0436 (8)	0.0490 (9)	−0.0110 (7)	0.0013 (7)	−0.0111 (7)
C3	0.0535 (10)	0.0558 (10)	0.0473 (9)	−0.0123 (8)	−0.0010 (7)	−0.0085 (7)
C4	0.0661 (12)	0.0776 (13)	0.0496 (10)	−0.0238 (10)	0.0056 (9)	−0.0142 (9)
C5	0.108 (2)	0.0939 (19)	0.0741 (15)	0.0040 (15)	0.0068 (14)	−0.0387 (14)
C6	0.119 (2)	0.126 (2)	0.0466 (12)	−0.0267 (19)	0.0001 (13)	−0.0040 (13)

Geometric parameters (Å, °)

S1—C1	1.6606 (15)	C3—H3B	0.97
N1—C1	1.3165 (19)	C4—C5	1.517 (3)
N1—C2	1.454 (2)	C4—C6	1.518 (3)
N1—H1	0.86	C4—H4	0.98
C1—C1^{i}	1.522 (3)	C5—H5A	0.96
C2—C3	1.515 (2)	C5—H5B	0.96
C2—H2A	0.97	C5—H5C	0.96
C2—H2B	0.97	C6—H6A	0.96
C3—C4	1.522 (2)	C6—H6B	0.96
C3—H3A	0.97	C6—H6C	0.96
C1—N1—C2	125.09 (14)	C5—C4—C6	110.9 (2)
C1—N1—H1	117.5	C5—C4—C3	111.70 (19)
C2—N1—H1	117.5	C6—C4—C3	110.33 (18)
N1—C1—C1^{i}	113.92 (16)	C5—C4—H4	107.9
N1—C1—S1	124.00 (12)	C6—C4—H4	107.9
C1^{i}—C1—S1	122.08 (14)	C3—C4—H4	107.9
N1—C2—C3	111.77 (13)	C4—C5—H5A	109.5
N1—C2—H2A	109.3	C4—C5—H5B	109.5
C3—C2—H2A	109.3	H5A—C5—H5B	109.5
N1—C2—H2B	109.3	C4—C5—H5C	109.5
C3—C2—H2B	109.3	H5A—C5—H5C	109.5
H2A—C2—H2B	107.9	H5B—C5—H5C	109.5

C2—C3—C4	113.83 (15)	C4—C6—H6A	109.5
C2—C3—H3A	108.8	C4—C6—H6B	109.5
C4—C3—H3A	108.8	H6A—C6—H6B	109.5
C2—C3—H3B	108.8	C4—C6—H6C	109.5
C4—C3—H3B	108.8	H6A—C6—H6C	109.5
H3A—C3—H3B	107.7	H6B—C6—H6C	109.5
C2—N1—C1—C1^{i}	−179.80 (15)	N1—C2—C3—C4	−178.18 (15)
C2—N1—C1—S1	0.4 (2)	C2—C3—C4—C5	−66.7 (2)
C1—N1—C2—C3	88.31 (19)	C2—C3—C4—C6	169.55 (19)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···S1^{i}	0.86	2.45	2.9452 (15)	118
N1—H1···S1^{ii}	0.86	2.80	3.4251 (14)	131
C2—H2B···S1^{ii}	0.97	2.99	3.4991 (18)	114

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

Fig. 1

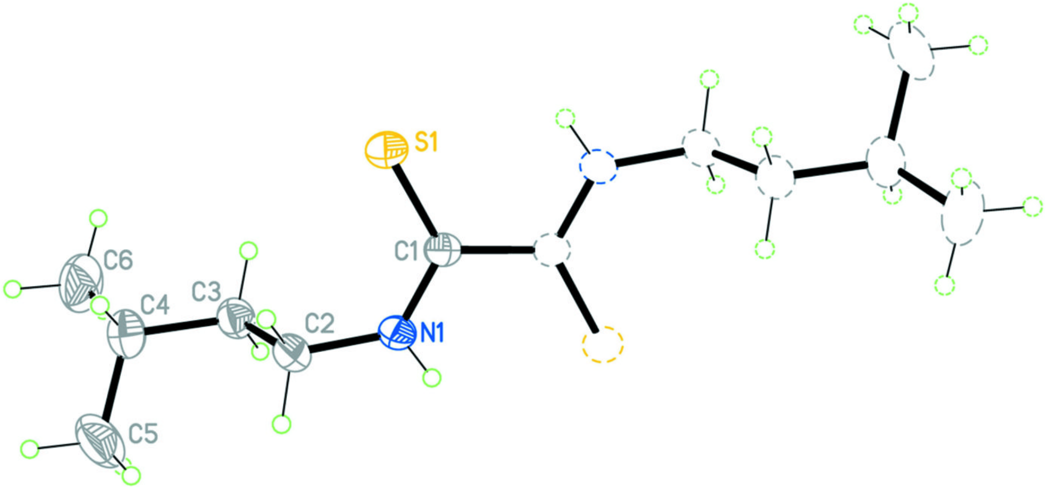


Fig. 2

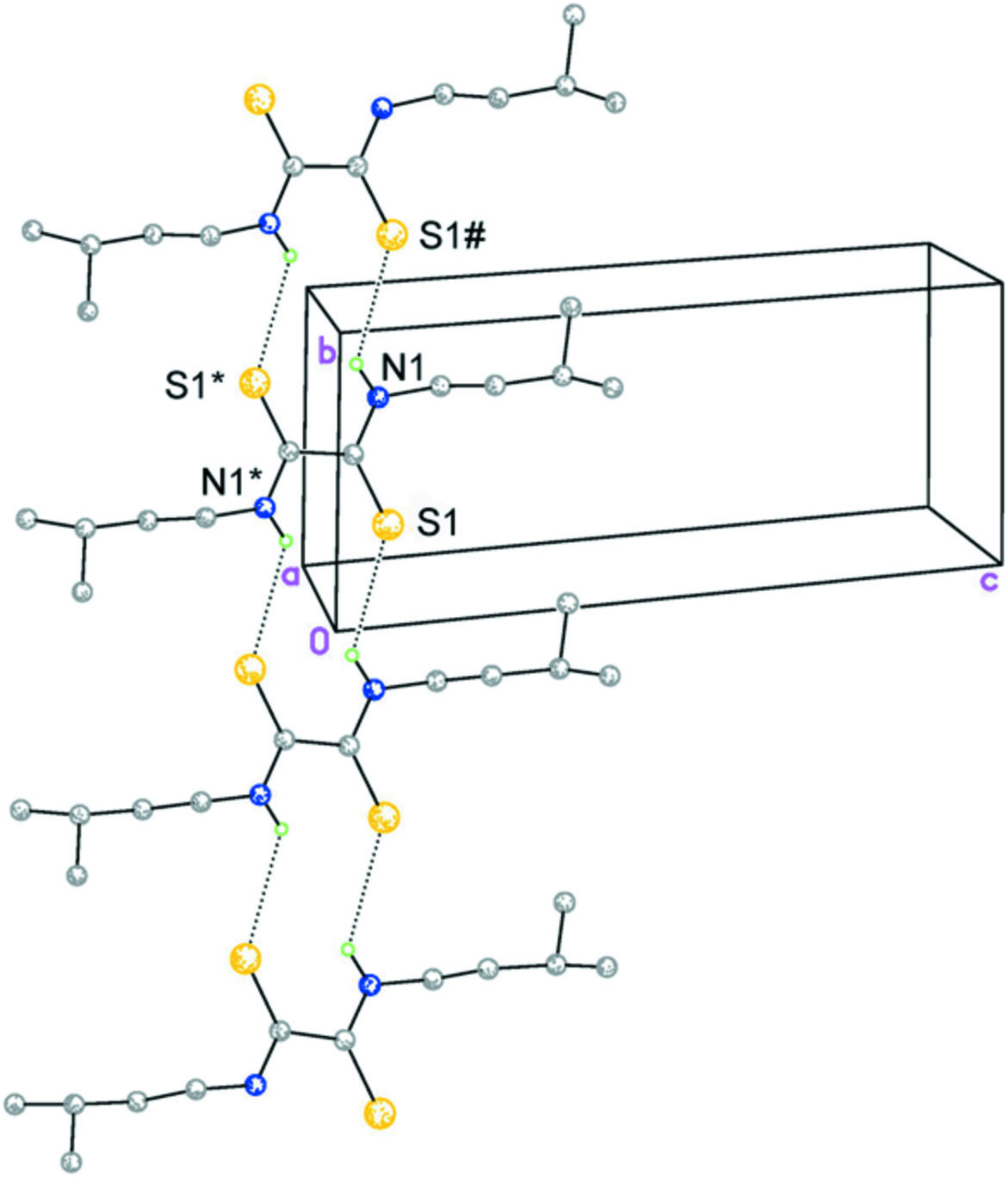


Fig. 3

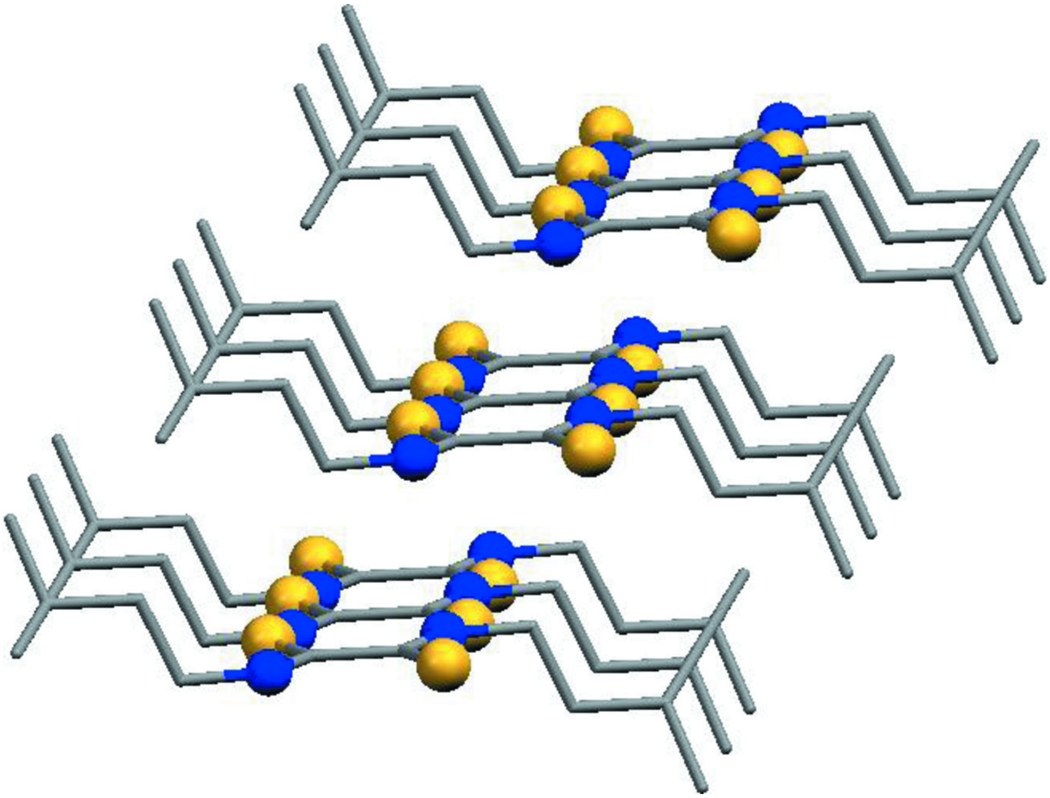
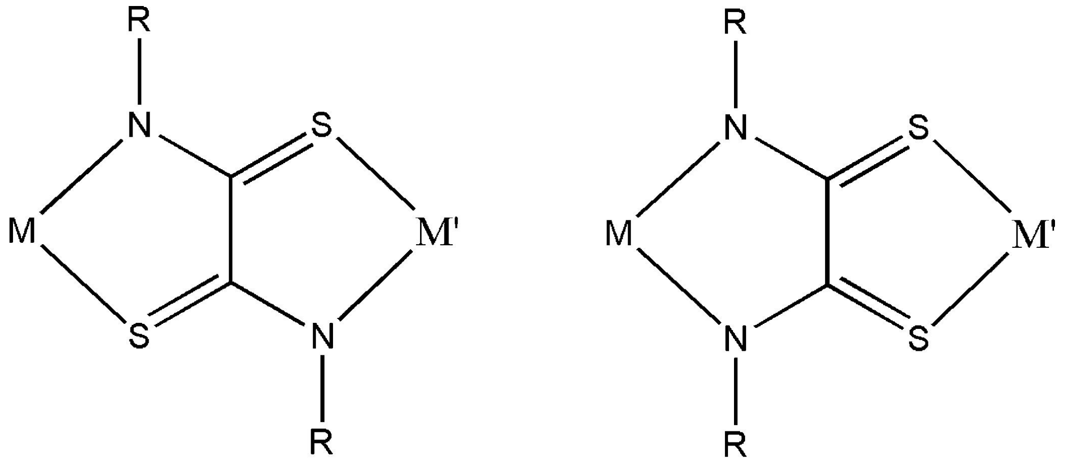


Fig. 4



N,S-N,S bridging mode

N,N-S,S bridging mode