# 4,5-Bis(benzylthio)-1,3-dithiole-2-thione compounds: crystal structures of [(*p*-XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)(*p*-XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)dmit: X=Y=OMe; X=Y=NO<sub>2</sub>; and X=OMe, Y=NO<sub>2</sub>]

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4,5-Bis(benzylthio)-1,3-dithiole-2-thiones,  $[(p-XC_6H_4CH_2)(p-XC_6H_4CH_2)dmit: X = Y = OMe$ (2); X=OMe, Y=NO<sub>2</sub> (3); and X=NO<sub>2</sub>] (4)] have been prepared from benzyl chlorides and [NEt<sub>4</sub>]<sub>2</sub>[Zn(dmit)<sub>2</sub>]. Isostructural compounds, **2** and **3**, crystallize in the triclinic space group  $P\overline{1}$  (Z = 2) with a = 5.2920(10), b = 10.537(2), c = 18.961(4) Å,  $\alpha = 102.79(3)$ ,  $\beta =$ 96.33(3),  $\gamma = 98.67(3)^{\circ}$  for **2**; a = 5.292(8), b = 10.528(12), c = 19.01(2) Å,  $\alpha = 102.74(9)$ ,  $\beta = 96.26(11)$ ,  $\gamma = 98.56(11)^{\circ}$  for **3**. Compound **4** also crystallizes in the space group  $P\overline{1}$ (Z = 4), with a = 9.296(8), b = 13.993(18), c = 16.186(4) Å,  $\alpha = 106.68(3)$ ,  $\beta = 89.63(3)$ ,  $\gamma = 99.38(6)^{\circ}$ . Molecular differences between **2** and **3**, on one hand, and **4**, on the other, arise in the disposition of the aryl rings relative to the dmit group. Short S---S contacts in **2** of 3.320(2) Å [S3---S3<sup>i</sup> (symmetry operation: i: -x + 1, -y + 1, -z)] and in **3** of 3.314(5)Å [S3---S3<sup>j</sup> (symmetry operation: i: -x + 1, -y + 1, -z)] and in **3** of 3.314(5)Å [S3---S2B contact of 3.516(5) Å links two independent molecules, A and B, into bimolecular units, which are further connected into chains by S2A---S5B<sup>i</sup> contacts (symmetry operation: i: x, y, z - 1) at 3.569(5) Å. C-H---O hydrogen bonds are also present in **3** and **4**.

**KEY WORDS:** 4,5-Bis(benzylthio)-1,3-dithiole-2-thiones; 1,3-dithiole-2-thione-4,5-dithiolates, dmit compounds.

# Introduction

Derivatives of 4,5-dimercapto-1,3-dithiole-2-thione (H<sub>2</sub>-dmit: **1**) have been extensively studied as heterocyclic compounds,<sup>1</sup> coordination compounds,<sup>2</sup> precursors of tetrathiafulvalene derivatives<sup>1,3,4</sup> and electronic conducting materials.<sup>5</sup> Many dmit compounds in the solid state are associated, particularly via S---S interactions but also, in appropriate compounds, via sulfur contacts with other elements, e.g., metals and oxygen, as illustrated by the compounds listed in the Cambridge Crystallographic Data Base.<sup>6</sup>

<sup>(1)</sup> Department of Chemistry, University of Aberdeen, Old Aberdeen, AB24 3UE, Scotland. 0044-1224-272930. Fax: 0044-1224-272921. E-mail: j.wardell@abdn.ac.uk The nature and extent of the the intermolecular contacts, and the arrays generated, vary with the dmit compound.

Intermolecular contacts have been investigated in three 4,5-bis(benzyl)thio-1,3-dithiole-2-thione compounds, namely 4,5-bis-(*p*-methoxybenzylthio)-1,3-dithiole-2-thione, (**2**), 4-(*p*-methoxybenzylthio)-5-(*p*-nitrobenzylthio)-1,3-dithiole-2-thione, (**3**), and 4,5-bis-(*p*-nitrobenzylthio)-1,3-dithiole-2-thione, **4**. The structures have been compared with that of previously reported 4,5-bis-(*p*-bromobenzylthio)-1,3dithiole-2-thione **5**.<sup>7</sup>

#### **Experimental section**

Melting points were measured on a Kofler hotstage and are uncorrected. NMR spectra were re-

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corded on a Bruker 250 MHz instrument, IR spectra on a Philips Analytical PU9800 FTIR instrumen and visible spectra on a Perkin Elmer Lambda 15 instrument. The compound, [NEt<sub>4</sub>]<sub>2</sub>[Zn(dmit)<sub>2</sub>], was obtained by a published procedure.<sup>8</sup>

# 4,5-Bis-(p-methoxybenzylthio)-1,3-dithiole-2-thione, 2

Solutions of p-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl (0.39 g, 2.50 mmol) in  $CH_2Cl_2$  (20 mL) and  $[NEt_4]_2[Zn(dmit)_2]$ (0.45 g, 0.63 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) were mixed and refluxed overnight. The solvent was removed to leave an oil, which was chromatographed on silica, using CH<sub>2</sub>Cl<sub>2</sub> as eluent. The title compound was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane as a red-brown colored crystalline solid, m.p. 119-122°C [lit. value<sup>9</sup> m.p. 95°C]; yield 0.36 g, 66%. Analysis. Found: C, 51.8; H, 4.3. Calculated for C<sub>19</sub>H<sub>18</sub>O<sub>2</sub>S<sub>5</sub>: C, 52.0; H, 4.1%. IR(KBr): v(C=S) 1058 cm<sup>-1</sup>. Vis (CH<sub>2</sub>Cl<sub>2</sub>):378, 521 nm. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz): *δ*: 3.87 [s, 6H, OMe], 3.90[s, 4H, CH<sub>2</sub>], 6.83[d, 4H, J 8.6], 7.15[d, 4H, J 8.6]. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 63MHz):  $\delta$  41.0[CH<sub>2</sub>], 55.4[Me], 127.8[C-2], 114.2[C-3], 130.3[C-1], 159.4[C-4], 137.5[C=C], 211.8[C=S].

# 4,5-Bis-(p-nitrobenzylthio)-1,3-dithiole-2-thione, 4

This was prepared similarly to **2** from p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl (0.43 g, 2.5 mmol) and [NEt<sub>4</sub>]<sub>2</sub>[Zn (dmit)<sub>2</sub>] (0.45 g, 0.63 mmol) as a red solid and was recrystallized from CHCl<sub>3</sub>/hexane, m.p. 105-6° C [lit. value<sup>9</sup> m.p. 102° C].

Analysis. Found: C, 44.0; H, 2.3; N, 6.1. Calculated for  $C_{17}H_{12}N_2O_4S_5$ : C, 43.6; H, 2.6; N, 6.0%. IR (KBr): v(C=S) 1061 cm<sup>-1</sup>. Vis (CH<sub>2</sub>Cl<sub>2</sub>): 374, 520 nm. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$ : 4.00[s, 4H, CH<sub>2</sub>], 7.40[d, 4H, J 8.6], 8.17[d, 4H, J 8.6]. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 63 MHz):  $\delta$ : 40.3 [CH<sub>2</sub>], 124.1[C-3], 129.9[C-2], 136.8[C=C], 143.2[C-1], 147.6[C-4], 209.9[C=S].

# 4-(p-Methoxybenzylthio)-5-(p-nitrobenzylthio)-1,3dithiole-2-thione, 3

Solutions of p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl (0.22 g, 1.25 mmol) and p-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl (0.20 g, 1.25 mmol) in  $CH_2Cl_2$  (20 mL) and  $[NEt_4]_2[Zn(dmit)_2]$  (0.90 g, 0.63 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) were mixed and refluxed overnight. The solvent was removed to leave an oil, which was chromatographed (preparative TLC) on silica using  $CH_2Cl_2$ /petroleum ether (40–60°C) (from 80:20 to 95:5 v:v) as eluents into three compounds: 2-4. Compound 3, the least mobile, was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> as a deep-red colored solid, m.p. 157°C. Analysis. Found: C, 47.5; H, 3.0; N, 3.1. Calculated for C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub>S<sub>5</sub>: C, 47.7; H, 3.3; N, 3.1%. IR (KBr): v(C=S) 1056, 1035 cm<sup>-1</sup>. Vis (CH<sub>2</sub>Cl<sub>2</sub>): 381, 522 nm. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250MHz): *δ*: 3.80[s, 3H, OMe], 3.94[s, 2H, CH<sub>2</sub>], 3.95[s, 2H, CH<sub>2</sub>], 6.85[d, 2H, J 8.6] & 7.15[d, 2H, J 8.6][anisyl-H], 7.37[d, 2H, J 8.6, H-2, nitrophenyl ring], 8.17[d, 2H, J 8.6, H-3, nitrophenyl ring]. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 63MHz):  $\delta$ : 40.0 & 40.5[CH<sub>2</sub>], 55.2[Me], 114.1[C-3, anisyl ring], 123.9[C-3, nitrophenyl ring], 127.3[C-1, anisyl ring], 129.7, 130.1[C-2, anisyl and nitrophenyl rings], 133.5[C=C], 140.0[C=C], 143.4[C-1, nitrophenyl ring], 147.4[C-4, nitrophenyl ring], 159.4, [C-4, anisyl ring], 210.7[C=S].

# Crystal structure determinations

All structures were determined using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å wavelength).

# Compound 2

Data were obtained at 293(2)K at the National Data Collection Centre of the EPSRC at Southampton. The instrument was an Enraf Nonius Kappa CCD area detector with an Enraf Nonius FR591 rotating anode as X-ray source. The phi-omega scan mode, filling the Ewald sphere, was employed. Data collection, and cell refinement and data reduction were accomplished with COLLECT<sup>10</sup> and DENZO,<sup>11</sup> respectively. An empirical correction for absorption was applied by means of SORTAV.<sup>12</sup> The structure was solved by direct methods, SHELXS86,13 and completed and refined with SHELXL97.14 Both methoxy groups exhibit disorder. The C and O atoms of the MeO group on C16 are distributed over two sites: C19A, 02A [site occupancy factor: 0.415(10)] and C19B, O2B [site occupancy factor: 0.585(10)]. Two occupied sites, C11A/C11B [site occupancy factors: 0.538(14)/0.462(14)], were calculated for the carbon atom of the other MeO group, on C8. All non-H

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were refined anisotropically and H were placed in calculated positions and refined with a riding model.

# Compound 3

Data were obtained at 298(2)K with a Nicolet P3 4-circle diffractometer operating in  $\theta$ -2 $\theta$  mode with variable scan rates in the range 5.33 (Ip < 150) to 58.6  $(Ip > 2500)^{\circ} 2\theta$ .min<sup>-1</sup> where Ip is the prescan intensity. The scan width was 2.4 to  $2.7^{\circ}$  in  $2\theta$ . For background count correction total background (two counts, one on either side of the Bragg angle) and peak scan count times were equal. Nicolet P3 software<sup>15</sup> was used for cell refinement and data collection and the local program RDNIC<sup>16</sup> for data reduction. No correction for absorption was applied. The structure was solved by direct methods, SHELXS86,13 and completed and refined with SHELXL97.14 The asymmetric unit is a single complete molecule. All non-H were refined anisotropically and H were placed in calculated positions and refined with a riding model.

## Compound 4

The unit cell and intensities data were collected at the National Data Collection Centre of the EPSRC at Cardiff at 293(2)K on a Delft Instrument FAST diffractometer using the routines ENDEX, REFINE and MADONL in the MADNES software<sup>17</sup> and processed using ABSMAD.<sup>18</sup> Procedural details were as described by Darr, *et al.*<sup>19</sup> The asymmetric unit consists of two crystallographically distinct molecules, which constitute a dimeric structural unit and are numbered in an identical manner but distinguished by suffices A and B. The nonhydrogen atoms were refined with anisotropic temperature factors and hydrogen atoms were allowed to ride on their attached carbon atoms with a common isotropic temperature factor. No absorption correction was applied.

All diagrams were obtained with ORTEP-3 for Windows<sup>20</sup> and ORTEX.<sup>21</sup> Crystal data and structure refinement details are listed in Table 1. Tables 2–4 list fractional coordinates and equivalent isotropic thermal parameters for the three compounds.

Compound	2	3	4
CCDC deposit no.	CCDC-1003/5697	CCDC-1003/5698	CCDC-1003/5699
Color	Red-brown	Deep-red	Red
Chemical formula	$C_{19}H_{18}O_2S_5$	$C_{18}H_{15}NO_3S_5$	$C_{17}H_{12}N_2O_4S_5$
Formula weight	438.63	453.61	468.59
Temperature, K	293(2)	298(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
Unit cell dimensions			
a (Å)	5.2920(10)	5.292(8)	9.296(8)
b (Å)	10.537(2)	10.528(12)	13.993(18)
c (Å)	18.961(4)	19.01(2)	16.186(4)
$\alpha$ (°)	102.79(3)	102.74(9)	106.68(3)
β(°)	96.33(3)	96.26(1)	89.63(3)
γ (°)	98.67(3)	98.56(11)	99.38(6)
Volume (Å)	1007.9(3)	1010(2)	1988(33)
Ζ	2	2	4
Density (calculated), mg/m <sup>3</sup>	1.445	1.491	1.566
Absorption coefficient, mm <sup>-1</sup>	0.586	0.593	0.610
Diffractometer/scan	Enraf Nonius	Nicolet P3 4-circle diffracto-	Delft Instrument FAST dif-
	RappaCCD area detector	meter 2.02.1.25.05	ifactometer
$\phi$ range for data collection (°)	2.02 to 27.44	2.02 to 25.05	2.22 to 24.83
Reflections measured	9661 4490 [D(:) 0.0001]/2505	3083	/001
Independent/observed reflections	$4480 [R(int) = 0.0691]/2565$ $[I > 2\sigma(I)]$	5582 [R(int) = 0.00/9]/1660 $[I > 2\sigma(I)]$	$4845 [R(int) = 0.0954]/1194 [I > 2\sigma(I)]$
Data/restraints/parameters	4480/0/246	3582/0/245	4845/0/505
Goodness-of-fit on $F^2$	1.049	0.997	0.588
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0758	R1 = 0.0681	R1 = 0.0570
	wR2 = 0.2235	wR2 = 0.1302	wR2 = 0.0976
R indices (all data)	R1 = 0.1277	R1 = 0.1623	R1 = 0.1915
(·····)	wR2 = 0.2583	wR2 = 0.1678	wR2 = 0.1188

#### Table 1. Crystal Data and Structure Refinement

	<i>x</i>	y	<i>z</i>	$\mid U(eq)^a$
<b>S</b> 1	11796(2)	5453(1)	1517(1)	72(1)
S2	12096(2)	2270(2)	1550(1)	86(1)
S3	7161(2)	4283(1)	393(1)	74(1)
S4	7379(2)	1591(1)	393(1)	73(1)
S5	3084(2)	2179(1)	-563(1)	81(1)
C1	9638(7)	4043(4)	999(2)	60(1)
C2	9718(7)	2795(5)	1015(2)	63(1)
C3	5732(7)	2664(4)	48(2)	62(1)
C4	9868(9)	6107(5)	2211(3)	79(1)
C5	9886(8)	5410(4)	2809(2)	67(1)
C6	7804(9)	4463(6)	2827(3)	85(2)
C7	7916(11)	3775(6)	3374(3)	100(2)
C8	10055(11)	4058(6)	3901(3)	88(2)
C9	12092(11)	5005(7)	3892(3)	95(2)
C10	12011(9)	5673(6)	3345(3)	86(2)
O1	10220(3)	3315(10)	4514(4)	194(3)
$C11A^b$	8390(2)	2525(10)	4519(5)	79(3)
$C11B^b$	12058(19)	3601(12)	4936(5)	71(3)
C12	10210(9)	1004(5)	1855(3)	88(2)
C13	11972(8)	412(5)	2315(3)	69(1)
C14	12121(13)	689(7)	3063(3)	105(2)
C15	13819(14)	111(7)	3480(3)	114(2)
C16	15199(11)	-725(6)	3133(4)	97(2)
C17	15008(10)	-1011(6)	2413(4)	92(2)
C18	13417(10)	-463(5)	1984(3)	83(1)
$O2A^b$	16530(2)	-1175(13)	3628(7)	101(2)
$C19A^b$	16470(4)	-820(2)	4336(11)	126(4)
$O2B^a$	17144(15)	-1611(9)	3373(5)	101(2)
$C19B^b$	17610(3)	-1191(15)	4107(8)	126(4)

<sup>*a*</sup> U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

<sup>b</sup> Site occupancy factors: C11A 0.538(14): C11B 0.462(14): O2A & C19A 0.415(10): O2B & C19B 0.585(10).

#### **Results and discussion**

The bis(benzyl)-dmit compounds, **2** and **4**, were obtained from reactions of  $[NEt_4]_2[Zn(dmit)_2]$  with the appropriate benzyl halide. The mixed benzyl derivative, **3**, was obtained, with the two symmetrical compounds, **2** and **4**, from a reaction mixture containing p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl and p-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl: separation of the three products was achieved using column chromatography. All bis(benzylthio)-dmit compounds are orange to brown colored solids, having a weak absorption in the visible region at ca 520 nm, with a stronger absorption at ca 370 nm. There were no significant differences in the  $\lambda$ max values for any of the bis(benzylthio)-dmit compounds prepared in this study. Values of v(C=S) in the IR spectra were in the narrow range of 1065-1055 cm<sup>-1</sup>.

## Crystal structures

The atom arrangements and the numbering system for 2-4 are shown in Figs. 1–3, respectively. Both methoxy groups in 2 exhibit disorder. The C and O atoms of the MeO group on C16 are distributed over two sites: C19a, O2a and C19b, O2b. Two sites, C11a/C11b, were calculated for the carbon atom of the other MeO group, on C8.

The geometric parameters within the dmit groups are similar in each of the bis(benzyl)dmit molecules, see Table 5. Compounds 2 and 3, are isostructural with the previously reported 5, but not, however, with 4. Two independent molecules, A and B, of 4 are present in the asymmetric unit, in contrast to only one in each of the other bis(benzyl)dmit compounds. The thione groups atoms, C3=S5, are in all cases out of the planes through the other dmit group atoms, i.e., the C=C and the attached S atoms: the distances the thione S atoms are out of the dmit plane

**Table 3.** Atomic Coordinates ( $\times$  10<sup>4</sup>) and Equivalent IsotropicDisplacement Parameters (Å<sup>2</sup>  $\times$  10<sup>3</sup>) for  $3^{a}$ 

	<i>x</i>	y	<i>z</i>	$\mid U(eq)^a$
<b>S</b> 1	-1786(3)	-458(2)	3487(1)	70(1)
S2	-2090(3)	2727(2)	3448(1)	85(1)
S3	2841(3)	714(2)	4607(1)	74(1)
S4	2625(3)	3408(2)	4602(1)	71(1)
S5	6909(3)	2827(2)	5559(1)	79(1)
C1	378(11)	960(6)	3989(3)	56(2)
C2	281(11)	2227(6)	3988(3)	59(2)
C3	4272(11)	2339(6)	4956(3)	60(2)
C4	140(13)	-1122(6)	2798(4)	78(2)
C5	124(12)	-418(6)	2198(3)	64(2)
C6	2165(13)	526(7)	2181(4)	77(2)
C7	2177(15)	1203(8)	1632(5)	92(2)
C8	-39(18)	911(8)	1115(4)	84(2)
C9	-2127(15)	-40(8)	1122(4)	94(2)
C10	-1981(14)	-687(7)	1671(4)	84(2)
N1	-110(2)	1643(10)	541(5)	118(3)
O1	1670(2)	2441(8)	511(5)	194(4)
O2	-2040(2)	1393(10)	100(5)	190(4)
C11	-230(13)	3993(7)	3137(4)	86(2)
C12	-1969(12)	4594(6)	2685(4)	66(2)
C13	-3436(13)	5466(7)	2999(4)	75(2)
C14	-5019(14)	6020(7)	2590(5)	91(2)
C15	-5187(17)	5727(9)	1858(6)	98(3)
C16	-3730(2)	4871(9)	1509(4)	114(3)
C17	-2173(17)	4304(7)	1936(5)	99(3)
O3	-6920(12)	6439(7)	1513(4)	157(3)
C18	-7170(2)	6063(11)	772(6)	214(7)

<sup>*a*</sup>U(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor.

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**Table 4.** Atomic Coordinates ( $\times$  10<sup>4</sup>) and Equivalent Isotropic Displacement Parameters ( $\mathring{A}^2 \times 10^3$ ) for 4<sup>a</sup>

	<i>x</i>	y	z	$\mid U(eq)^a$
S1A	-354(3)	5873(2)	2679(2)	71(1)
S2A	607(3)	3543(3)	1994(2)	67(1)
S3A	1295(4)	6021(2)	4308(2)	82(1)
S4A	2038(3)	4057(2)	3774(2)	65(1)
S5A	2858(4)	5311(3)	5551(2)	89(1)
C1A	675(10)	5296(8)	3250(7)	50(3)
C2A	1009(10)	4369(8)	3001(7)	51(3)
C3A	2178(11)	5126(8)	4601(7)	57(3)
C4A	881(12)	7010(9)	2701(9)	105(5)
C5A	300(13)	7548(10)	2122(10)	64(4)
C6A	531(13)	7279(10)	1261(10)	80(5)
C7A	70(13)	7822(12)	744(9)	82(5)
C8A	-663(13)	8574(9)	1100(9)	52(4)
C9A	-941(12)	8846(9)	1953(9)	61(4)
C10A	-423(12)	8325(10)	2447(7)	58(4)
N1A	-1138(12)	9184(11)	562(8)	74(4)
O1A	-942(10)	8850(8)	-207(6)	104(4)
O2A	-1707(11)	9880(8)	892(8)	117(4)
C11A	-781(10)	2552(8)	2173(7)	61(4)
C12A	-250(11)	2060(8)	2808(8)	47(3)
C13A	781(10)	1433(8)	2601(7)	42(3)
C14A	1295(11)	988(8)	3188(9)	54(4)
C15A	766(13)	1216(10)	3988(9)	56(4)
C16A	-240(13)	1791(9)	4232(8)	66(4)
C17A	-780(12)	2221(9)	3636(9)	68(4)
N2A	1322(13)	790(10)	4610(8)	77(4)
O3A	2044(10)	134(8)	4356(7)	106(4)
O4A	1061(11)	1127(8)	5357(7)	112(4)
S1B	5357(3)	4100(2)	7238(2)	76(1)
S2B	4358(3)	6397(3)	7666(2)	65(1)
S3B	3709(4)	3948(2)	8815(2)	82(1)
S4B	2930(3)	5903(2)	9220(2)	71(1)
S5B	2157(4)	4683(3)	10411(2)	94(1)
C1B	4295(10)	4668(9)	8076(7)	57(3)
C2B	4027(11)	5598(8)	8277(7)	55(4)
C3B	2751(12)	4789(9)	9494(9)	105(6)
C4B	4145(12)	2928(9)	6728(7)	95(5)
C5B	4669(12)	2443(10)	5870(9)	59(4)
C6B	4378(13)	2728(10)	5163(10)	73(3)
C7B	4778(13)	2235(10)	4351(9)	72(4)
C8B	5574(12)	1470(10)	4279(8)	51(3)
C9B	5945(12)	1171(8)	4966(8)	56(4)
C10B	5453(12)	1672(9)	5769(7)	57(4)
N1B	5990(12)	902(10)	3415(8)	72(4)
O1B	5774(11)	1224(8)	2813(6)	113(4)
O2B	6617(10)	208(7)	3372(6)	96(4)
C11B	5701(10)	7391(8)	8315(7)	56(3)
C12B	5205(10)	7896(8)	9188(7)	37(3)
C13B	4168(11)	8537(8)	9271(7)	47(3)
C14B	3683(11)	8984(8)	10069(8)	47(3)
C15B	4175(12)	8805(9)	10754(9)	48(3)
C16B	5151(14)	8194(9)	10721(8)	68(4)
C17B	5716(12)	7745(9)	9943(10)	71(4)
N2B	3634(12)	9249(9)	11597(8)	75(4)
O3B	2954(10)	9920(7)	11645(6)	105(4)
O4B	3896(10)	8946(8)	12190(6)	101(4)

<sup>*a*</sup>U(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor.



**Fig. 1.** Atom arrangements and numbering system for **2**. H-atoms are omitted for clarity, as are disordered atoms, C11b, O2b, and C19b. Probability ellipsoids drawn at 20%.



Fig. 2. Atom arrangements and numbering system for 3. H-atoms are omitted for clarity. Probability ellipsoids drawn at 20%.



**Fig. 3.** The common numbering system used for the two independent molecules, A and B, of **4**. H-atoms have been omitted for clarity.

are 0.0086(2) Å in **2**, 0.079(4) Å in **3**, and 0.135(6) (molecule A) and 0.156(6) Å in **4**.

Conformational differences between **2**, **3**, and **5**, on one hand, and **4**, on the other, are indicated by the angles between the planes of the dmit group and aryl rings: for example, the dmit plane makes angles

			4	
	2	3	molecule A	molecule B
S3-C1	1.732(4)	1.745(6)	1.766(10)	1.802(11)
S4-C2	1.754(4)	1.742(7)	1.770(10)	1.816(11)
S3-C3	1.707(4)	1.716(6)	1.774(10)	1.725(11)
S4-C3	1.721(4)	1.725(6)	1.684(10)	1.723(10)
S5-C3	1.653(4)	1.644(7)	1.600(10)	1.618(12)
C1-C2	1.329(6)	1.343(8)	1.331(11)	1.313(12)
S1-C1	1.752(4)	1.754(7)	1.764(10)	1.751(10)
S2-C2	1.759(4)	1.749(6)	1.708(11)	1.685(11)
S1-C4	1.832(5)	1.827(7)	1.795(11)	1.809(12)
S2-C11		1.783(7)	1.820(10)	1.791(11)
S2-C12	1.782(5)			
S5-C3-S4	123.6(3)	123.7(4)	126.8(6)	123.0(8)
S5-C3-S3	123.6(3)	124.0(4)	126.0(6)	124.1(6)
C3-S4-C2	97.0(2)	97.9(3)	100.9(5)	100.3(5)
C3-S3-C1	98.1(2)	98.2(3)	98.9(5)	98.9(5)
S4-C2-C1	115.9(3)	115.8(4)	115.1(9)	112.9(9)
C2-C1-S3	116.0(3)	115.6(4)	115.1(8)	116.8(8)
S3-C3-S4	112.8(2)	112.3(3)	110.0(6)	110.8(6)
C2-C1-S1	126.7(3)	127.7(4)	128.6(9)	126.9(9)
C1 - C2 - S2	125.4(3)	124.2(5)	124.2(9)	126.1(9)

of  $61.17(15)^{\circ}$  and  $42.14(15)^{\circ}$  with the aryl planes in **2**, 61.1(2)° [*p*-MeOC<sub>6</sub>H<sub>4</sub>] and 42.4(2)° [*p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>] in 3, in contrast to  $43.1(3)^{\circ}$  and  $31.6(3)^{\circ}$  in molecule A, and 42.0(4)° and 32.8(3)° in molecule B of compound 4. The angles between the aryl planes, 83.88(16) and  $83.9(2)^\circ$ , in 2 and 3, respectively, are markedly different from those in 4, 14.5(6) (molecule A) and  $11.7(6)^{\circ}$ (molecule B). In 2, 3, and 5, both benzyl groups are directed away from the dmit moiety to provide an extended configuration, whereas in 4, only one benzyl extends away from the dmit unit, the other is folded back upon it. The change in conformation from the extended form of 2, 3, and 5 to the semifolded from of **4** is brought about by rotation of a benzyl group about the appropriate S-CH<sub>2</sub> bond, on average, 138.4°, as shown by the torsion angles in Table 6.

Short S---S contacts in **2** of 3.320(2) Å [S3---S3<sup>*i*</sup> (symmetry operation: i: -x + 1, -y + 1, -z] and in



**Fig. 4.** The cell of **3** viewed down *a* (up into page) showing S---S contacts, but not H-bonds. The direction of b\* and c\* are indicated. Non-H-atoms are shown as 20% ellipsoids: H-atoms are omitted for clarity.

**3** of 3.314(5) Å [S3---S3<sup>*i*</sup> (symmetry operation: *i*: -x + 1, -y, -z + 1] link the molecules into pairs: Figure 4 illustrates the S---S interactions in **3**. The equivalent S---S distance in **5** is 3.36(1) Å. There are no other S---S contacts in **2**, **3**, and **5** less than the van der Waals radii sum of 3.70 Å.<sup>22</sup>

An intermolecular Br----Br separation of 3.65(1) Å is present in 5;<sup>7</sup> this distance is at the lower end of the range of the sum of the van der Waals radii for two Br atoms – between 3.60 and 4.00 Å.<sup>22</sup> In 2, which, as mentioned above, is isostructural with 5, there are no intermolecular contacts less than appropriate van der Waals radii sums. In 3, also isostructural with 2, intermolecular contacts involving C9 and O2  $\|$  [C9---O2<sup>*ii*</sup> = 3.553(14) Å, H9---O2<sup>*ii*</sup> = 2.65 Å,  $\angle$ C9-H9---O2<sup>*ii*</sup> =  $163.7^{\circ}$  (symmetry operation: *ii*: -x + 1, -y + 1, -z)] occurs. While H-bonds between aryl-H and O atoms of nitro groups are well-established,<sup>23,24</sup> the C---O distance in this interaction in **3** appears at the limits of a H-bonding interaction. A slightly shorter contact involves C18 and O2<sup>iii</sup> [3.498(13)] Å: (symmetry operation: *iii*: -x + 1, -y + 1

Table 6.	Selected	Torsional	Angles (	(°)	in	2-4
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2		3			4	
C2-S2-C12-C13	178.8(4)	C2-S2-C11-C12	-177.4(5)	C1-S1-C4-C5	molA mol B	171.2(10) 165.6(9)
C1-S1-C4-C5	80.5(4)	C1-S1-C4-C5	-79.7(5)	C2-S2-C11-C12	molA molB	-57.9(9) -58.7(9)



Fig. 5. The cell of 3 viewed down a (down into page) showing S---S contacts, but not H-bonds. The direction of b\* and c\* are indicated. Non-H-atoms are shown as 20% ellipsoids: H-atoms are omitted for clarity. Representative molecules A and B are indicated.

(1, -z)] i.e., with the methoxyl group. The fact that the three compounds, 2, 3, and 5, are isostructural indicates that the individual substituents have no specific role in the structural arrangements.

In contrast to the situation in 2, 3, and 5, two distinct S---S intermolecular contacts occur in 4 at distances less than the van der Waals radii sum (see Fig. 5). An S5A---S2B contact of 3.5116(5) Å links the two independent molecules, A and B, into a bimolecular unit, which are further connected into chains, propagated in the c direction, by S2A---S5B<sup>i</sup> contacts (symmetry operation: *i*: x, y, z-1) at 3.569(5) Å. There are much more clear-cut C-H---O hydrogen bonds present in the crystal structure of 4, see Table 7, compared to that in 3.

# Conclusions

The differences in the molecular structure of 4. compared to those of 2, 3, and 5, could arise from the greater polarity or the greater steric requirements of the nitro group, or even to both factors: the strongly electron-rich oxygens will result in considerable electrostatic repulsion for a close approach of the two nitro groups. Either factor will provide resistance to the aryl groups in 4 occupying the same space as that taken up by the *p*-substituted-aryl groups in molecules, 2, 3, and 5: hence a conformation with a greater separation of the two aryl groups will be preferred for 4. That 2, 3, and 5 are isostructural indicates that individual factors, namely Br---Br interactions in 5 and H-bonds in 3, if present at all, cannot be structurally significant. Furthermore, there is no specific interaction between the electron-rich methoxyphenyl ring and the electron-poor nitrophenyl ring in 3.

Molecules of 2, 3, and 5 are linked into moleculedimers by a single ring-S---ring-S contact, in contrast to the situation in 4 in which two longer and distinct S---S contacts, both involving exocyclic-S---thione-S contacts, result in chains of molecules formed from 4A-4B pairs. With different molecular conformations, it is not difficult to envisage that differences in intermolecular contacts will arise. The folding back of a benzyl group in 4 allows more ready access to the exocyclic-S atoms. In all cases, the individual S---S contacts constitute at best weak interactions.

The H-bonds, involving the nitro group oxygen atoms in 4, and to a lesser extent in 3, augment the S---S interactions in forming the molecular assembly in the crystalline state.

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Table 7. Intermolecular Hydrogen Bonds in 4					
С-нО	d(HO) Å	D(CO) Å	[C-H0		
C10A-H10AO4A <sup>iii</sup>	2.56	3.483(15)	175.0		
C14A-H14AO3B <sup>iv</sup>	2.40	3.072(15)	128.9		
C9B-H9BO3A <sup>v</sup>	2.40	3.214(14)	145.6		
C13B-H13BO1B <sup>vi</sup>	2.66	3.484(14)	148.2		
C14B-H14BO2A <sup>vii</sup>	2.54	3.276(14)	136.1		

olecular Hydrogen Bonds in A

Note: symmetry operations: <sup>iii</sup>: -x, -y + 1; <sup>iv</sup>: x, y - 1, z - 1; <sup>v</sup>: -x + 1, -y, -z + 1;<sup>vi</sup>: -x + 1, y + 1, -z + 1;<sup>vii</sup>: -x, -y + 2, -z + 1.

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