

Nitroso derivatives of 1,3-dithiol-2-ylidene stabilised by intramolecular oxygen ··· sulfur interactions: synthesis and X-ray crystal structures

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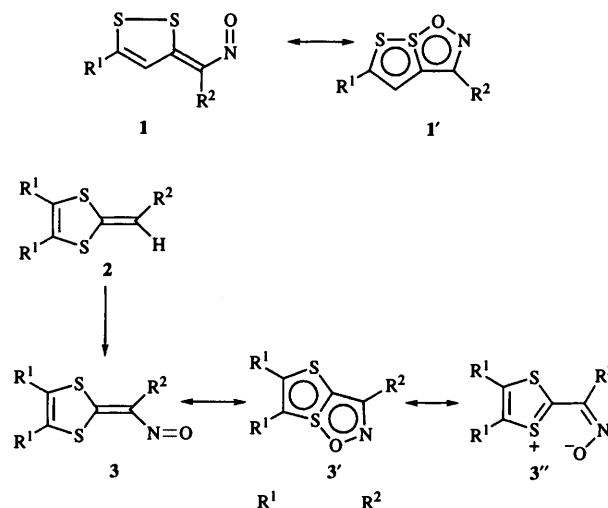
A series of 2-(nitrosomethylene)-1,3-dithiole derivatives **3** have been synthesised, and X-ray crystal structures of compounds **3g**, **3h** and **3l** have been obtained. The coplanarity of the dithiole ring and the nitroso group in all three compounds favours π -conjugation, and short intramolecular oxygen ··· sulfur contacts (*ca.* 2.4 Å) occur between the nitrosyl oxygen and a sulfur atom of the dithiole ring; these structural features explain the stability and unreactivity of the series of compounds **3**.

Vinylnitroso compounds are generally highly reactive species which cannot be isolated, evidence for their intermediacy being provided by intermolecular trapping reactions with nucleophiles or in Diels–Alder cycloadditions.¹ Stabilisation of vinylnitroso groups has been achieved in a few systems by virtue of strong conjugative interaction between the C=C and N=O double bonds,² or, more extensively, by participation of the nitroso group in non-bonded O···S intramolecular interactions, where considerable π -electron delocalisation and additional heteroaromatic stability can result, *e.g.* in 1-oxa-6,6a-dithia-2-azapentalene† derivatives **1**.³ This topic is the subject of renewed interest in 1,2-dithiole-3-thione derivatives functionalised in the 5-position, which are of pharmaceutical importance.^{3g}

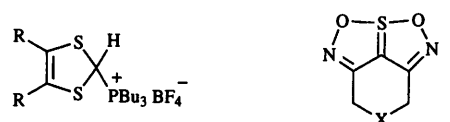
We were attracted by a report from Lakshmikantham and Cava that a nitroso derivative of 1,3-dithiol-2-ylidene, could be obtained by nitrosation of **2a** and isolated as a stable solid which was deoxygenated by phosphines to give products derived from intermediary nitrenes: surprisingly, the nitroso compound was represented as the transoid structure **3a**, and possible heteropentalene or resonance-stabilised structures **3'** or **3''**, respectively, were not discussed.⁴ It was, therefore, of interest to explore in more detail the synthesis and structure of nitroso derivatives of the 2-methylene-1,3-dithiole system. While our work was in progress, Gowenlock *et al.* reported some new analogues of **3a**, and obtained their coordination compounds with palladium chloride.⁵ Variable temperature NMR studies established that the free energy barrier to rotation about the exocyclic C=C bond of **3a** was low, which was ascribed to a contribution from a dipolar resonance canonical structure **3''**.⁵ As before,⁴ a possible heteropentalene structure **3'** was not mentioned.⁵ Herein we report the results of our study on the synthesis of new derivatives of system **3**, and we describe the X-ray crystal structure of three novel nitrosated products **3g**, **3h** and **3l**.

Results and discussion

In order to explore the generality of the nitrosation reaction, and to obtain derivatives of system **3** suitable for single crystal X-ray analysis, a range of 1,3-dithiol-2-ylidene derivatives **2b–3m** was prepared by Wittig reaction of phosphoranes **4**,⁶ **5**⁷ or **6**⁸ with the appropriate aldehyde derivative. Nitrosation of compounds **2b–m** was then attempted using the method reported

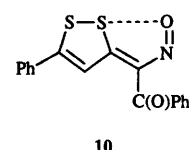
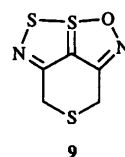


a	CO ₂ Me	C ₆ H ₅
b	CO ₂ Me	2-NO ₂ -C ₆ H ₄
c	CO ₂ Me	2,4-(NO ₂) ₂ -C ₆ H ₃
d	CO ₂ Me	2,6-Cl ₂ -C ₆ H ₃
e	CO ₂ Me	2-CF ₃ -C ₆ H ₄
f	CO ₂ Me	5-NO ₂ -2-furyl
g	CO ₂ Me	2-pyridyl
h	CO ₂ Me	C(O)Me
i	CO ₂ Me	CHO
j	Me	C ₆ H ₅
k	Me	2,4-(NO ₂) ₂ -C ₆ H ₃
l	MeS	2-pyridyl
m	MeS	C ₆ H ₅



4 R = CO₂Me
5 R = Me
6 R = MeS

7 X = CMe₂
8 X = S, SO, SO₂



† IUPAC name: [1,2]dithio[2,3-*b*][1,2,5]oxathiazole.

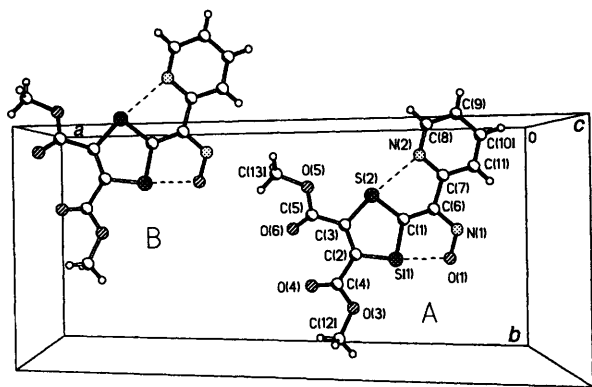


Fig. 1 Asymmetric unit of **3g**; projection on the (1 0 -2) plane (twinning plane). Molecules A and B have the same numbering scheme, shown for the former.

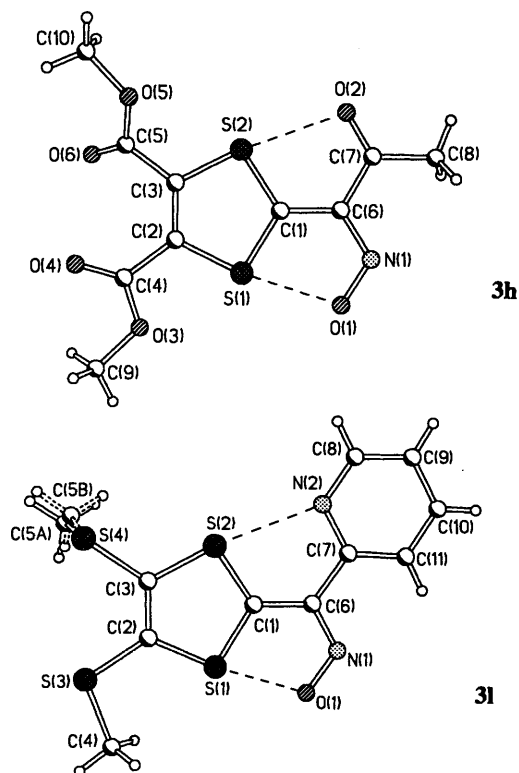


Fig. 2 Molecular structures of **3h** and **3l**, showing the methyl group disorder in **3l**

previously (isoamyl nitrite in dichloromethane at room temperature).⁴ The gradual conversion of the typical yellow or orange solution of compounds **2** into a bright green reaction solution was diagnostic of the formation of the nitrosated product. By this method the nitrosated products **3c, d, g-i, k-m** were obtained as air-stable green solids in 27–70% yields. Analogous nitroso compounds **3b** and **e** were formed as judged by the green colouration of the reaction solution and TLC evidence, but they could not be obtained as solid products, and attempted purification by column chromatography on silica or alumina of the crude green oil which was isolated, resulted in decomposition to a multitude of unidentified products. Pure product could not be obtained from the attempted nitrosation of **2f** and **2j**; mass spectrometric data suggested that in both cases the products were a mixture of the nitroso derivatives **3f** and **3j** and the corresponding nitro compounds.

From consideration of the series of derivatives **3a-m**, it became apparent that the stability of the nitrosated compounds **3** is increased by the presence of an electron-withdrawing substituent either on the dithiole ring or on the methylene carbon atom (or both), e.g. derivatives **3a** and **3k** are stable, whereas **3j** is unstable.

Table 1 Relevant bond distances in molecules **3**

Bond	3g		3h	3l
	A	B		
S(1)–C(1)	1.732(4)	1.720(4)	1.707(2)	1.730(2)
S(2)–C(1)	1.712(4)	1.720(4)	1.705(2)	1.703(2)
S(1)–C(2)	1.755(4)	1.745(4)	1.746(2)	1.758(2)
S(2)–C(3)	1.732(4)	1.729(4)	1.723(2)	1.736(2)
C(2)–C(3)	1.343(5)	1.347(5)	1.348(3)	1.347(3)
C(1)–C(6)	1.385(5)	1.409(5)	1.409(3)	1.417(2)
N(1)–C(6)	1.345(5)	1.336(5)	1.357(3)	1.345(2)
O(1)–N(1)	1.266(4)	1.288(4)	1.264(3)	1.276(2)
S(1)···O(1)	2.359(3)	2.353(3)	2.432(3)	2.359(1)
S(2)···X(2) ^a	2.698(3)	2.682(3)	2.611(3)	2.734(2)

^a X = N (**3g**, **3l**), O (**3h**).

Single crystals were obtained for compounds **3g**, **3h** and **3l** and X-ray structural analysis revealed similar molecular geometries (see Figs. 1 and 2, Table 1). There are two independent molecules of **3g** in the unit cell. In molecule A the dithiole–C(6)–pyridyl system is essentially planar, and the nitrosyl atoms N(1) and O(1) deviate from its plane by 0.12 and 0.14 Å, respectively; in molecule B, this deviation is even smaller, 0.06 and 0.05 Å, respectively, while the dithiole and pyridyl planes form a dihedral angle of 3°. In both molecules A and B, the methoxycarbonyl substituents at C(2) and C(3) are similarly inclined to the dithiole plane (by 22 and 32° in A, and by 21 and 35° in B). In the structure of the acetyl derivative **3h**, the dithiole ring, nitrosyl and carbonyl groups lie in one plane within ±0.03 Å, with C(8) tilted out of this plane by 0.13 Å; the methoxycarbonyl substituents at C(2) and C(3) are inclined to this plane by 21 and 40°, respectively. In the structure of compound **3l**, the dithiole ring, S(3), S(4), C(4), C(6), N(1) and O(1) atoms are coplanar; the disordered C(5) atom deviates from their mean plane by 1.78 Å in A and 1.58 Å in B, and the pyridyl ring is inclined to that plane by 7.2°.

Thus, the conformations of all three compounds favour π -conjugation and imply short intramolecular contacts of S(1) with the nitrosyl oxygen atom O(1), and of S(2) with the pyridyl N(2) atom in **3g** and **3l** or with the carbonyl O(2) atom in **3h**. The S(1)···O(1) distances (see Table 1) lie well within the range (2.0–3.0 Å) of donor–acceptor interactions (shortened non-valent contacts).⁹ On the other hand, they are longer than the symmetrical hypervalent S–O bonds in compounds **7** (1.88 Å)¹⁰ and **8** (1.85 Å),¹¹ and the sulfur–nitrosyl contacts in **9**¹² and **10**^{3d} (S–O 2.09 and 2.03 Å, respectively), which are regarded as intermediate between hypervalent and non-bonded interactions.⁹

In the nitrosyl groups of **3**, the N(1)–O(1) bonds are longer, and the C(6)–N(1) shorter than usual in C(sp²)-bound nitrosyls¹³ (1.14–1.23 and 1.41–1.45 Å, respectively) without extra interactions. However, the distortion is not as large as in compounds **7–9**, where the N–O distances (1.34–1.36 Å) are closer to the standard single bond length of 1.40 Å and the C–N (1.31–1.32 Å) to that of the double bond (1.28 Å).¹⁴

The relative weakness of S(1)···O(1) interactions in the structures of **3** is not surprising, as in linear X–S···O systems the S···O interactions are always much weaker if X=C rather than a heteroatom (S, O, N).⁹ Nevertheless, the C(2)–S(1) distances in **3** are longer by 0.02 Å than the C(3)–S(2) distances, indicating that the nitrosyl substituent affects the electron distribution in the 1,3-dithiole ring.

It is noteworthy that the S(2)···O(carbonyl) interaction in compound **3h** is much weaker than the S(1)···O(nitrosyl) interaction. The same trend is seen in compound **10**, where a nitrosyl group expels the carbonyl group from interaction with S altogether.^{3d} Equally weaker are the S(2)···N(2) interactions in **3g** and **3l**, taking into account the proximity of the van der Waals radii of O and N (1.4 and 1.5 Å).¹⁵ A heteropentalene structure

3' is, therefore, not a major contributing canonical structure, and the system is better represented by structure 3'.

In **3l**, molecules form stacks parallel to the direction of the *x* axis, with an interplanar separation of *ca.* 3.55 Å and almost maximum (head-to-tail) overlap. In the two other structures, **3g** and **3h**, the orientation of the CO₂Me groups prevents efficient stacking.

Attempted reactions of the nitroso or vinylnitroso units of compounds **3** have proved unsuccessful, which is consistent with the stabilised cyclic structures revealed by X-ray analysis. Compound **3g** was unreactive with cyclohexene, dimethyl acetylenedicarboxylate and dihydropyran in refluxing chloroform; decomposition occurred in refluxing toluene. Compound **3c** was unreactive with dimethylbutadiene at room temperatures; at higher temperatures (*e.g.* refluxing toluene) an intractable product mixture was formed. Attempted thionation of the nitroso group of compound **3a** (phosphorus pentasulfide, toluene, at temperatures between 0 °C and reflux) leads to either no reaction or decomposition.

In conclusion, we have synthesised a range of nitroso derivatives of 2-ylidene-1,3-dithioles **3** and established by single crystal X-ray studies of three derivatives that their unusually high stability is a consequence of extended π -conjugation and a short intramolecular oxygen \cdots sulfur contact.

Experimental

General methods and instrumentation

These are the same as those reported recently.¹⁶ All reactions were performed under a dry nitrogen atmosphere.

Preparation of [4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]methane derivatives **2b–h**. General Procedure.

To a stirring solution of Wittig reagent **4**⁶ (2.0 g, 3.96 mmol) and the appropriate aldehyde (3.96 mmol) in dry tetrahydrofuran (50 ml) was added triethylamine (5 ml, excess) and the mixture was stirred at 20 °C for 20 h. The solvent was removed under vacuum and the resulting solid was purified by column chromatography on silica gel using a dichloromethane–hexane mixture as eluent, and recrystallised from dichloromethane–methanol (1:10 v/v). The following derivatives were thereby obtained.

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene](2-nitrophenyl)methane **2b** yellow crystals (82% yield), mp 115.5–116 °C (Found: C, 47.2; H, 3.1; N, 4.0. C₁₄H₁₁NO₆S₂ requires C, 47.6; H, 3.1; N, 4.0%) *m/z* (EI) 353 (M⁺); ν_{\max} (KBr)/cm⁻¹ 1737, 1716, 1592, 1571, 1543, 1522, 1343 and 1257; δ_{H} (CDCl₃) 7.37 (m, 4 H), 6.94 (s, 1 H), 3.87 (s, 3 H) and 3.83 (s, 3 H).

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene](2,4-dinitrophenyl)methane **2c** orange crystals (80% yield), mp 156–157 °C (Found: C, 42.5; H, 2.5; N, 7.0. C₁₄H₁₀N₂O₈S₂ requires C, 42.1; H, 2.5; N, 7.0%) *m/z* (EI) 398 (M⁺); ν_{\max} (KBr)/cm⁻¹ 1733, 1726, 1588, 1540, 1530, 1512, 1335 and 1257; δ_{H} (CDCl₃) 8.83 (d, *J* 2.98 Hz, 1 H), 8.43 (dd, *J* 11 and 3.00 Hz, 1 H), 7.70 (d, *J* 11 Hz, 1 H), 7.08 (s, 1 H), 3.91 (s, 3 H) and 3.88 (s, 3 H).

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene](2,6-dichlorophenyl)methane **2d** yellow oil (87% yield), *m/z* (EI) 377 (M⁺) (HRMS found 375.93927; C₁₄H₁₀Cl₂O₄S₂ requires 375.93976); ν_{\max} (neat)/cm⁻¹ 1728, 1591, 1433 and 1258; δ_{H} (CDCl₃) 7.25 (m, 3 H), 6.33 (s, 1 H), 3.87 (s, 3 H) and 3.80 (s, 3 H).

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene][2-(trifluoromethyl)phenyl]methane **2e** yellow crystals (64% yield), mp 117.5–118.5 °C (Found: C, 47.7; H, 2.9. C₁₅H₁₁F₃O₄S₂ requires C, 48.0; H, 3.0%) *m/z* (EI) 376 (M⁺); ν_{\max} (KBr)/cm⁻¹ 1730, 1658, 1309, 1260, 1222 and 1029; δ_{H} (CDCl₃) 7.32–7.65 (m, 4 H), 6.67 (q, *J*_{H-F} 1.98 Hz, 1 H), 3.89 (s, 3 H) and 3.84 (s, 3 H).

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene](5-nitro-2-furyl)methane **2f** orange solid (90% yield), mp 111.5–112.0 °C

(Found: C, 41.8; H, 2.7; N, 4.0. C₁₂H₉NO₇S₂ requires C, 42.0; H, 2.6; N, 4.1%) *m/z* (EI) 343 (M⁺); ν_{\max} (KBr)/cm⁻¹ 1731, 1716, 1595, 1363 and 1255; δ_{H} (CDCl₃) 7.39 (d, *J* 3.90 Hz, 1 H), 6.41 (s, 1 H) 6.30 (d, *J* 3.9 Hz, 1 H), 3.91 (s, 3 H) and 3.89 (s, 3 H).

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene](2-pyridyl)methane **2g** orange crystals (89% yield), mp 145.5–146.5 °C (Found: C, 50.5; H, 3.6; N, 4.6. C₁₃H₁₁NO₄S₂ requires C, 50.5; H, 3.6; N, 4.5%) *m/z* (EI) 338 (M⁺); ν_{\max} (KBr)/cm⁻¹ 1739, 1716, 1582, 1523, 1467 and 1226; δ_{H} (CDCl₃) 8.64 (dd, *J* 4.34, 0.60 Hz, 1 H), 7.60 (td, *J* 4.36 and 1.72 Hz, 1 H), 7.00 (m, 2 H), 6.63 (s, 1 H), 3.89 (s, 3 H) and 3.86 (s, 3 H).

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]propan-2-one **2h** yellow solid (89% yield), mp 134–135 °C (Found: C, 43.7; H, 3.4. C₁₀H₁₀O₅S₂ requires C, 43.8; H, 3.7%) *m/z* (EI) 274 (M⁺); ν_{\max} (KBr)/cm⁻¹ 1735, 1711, 1636, 1580, 1490, 1433 and 1250; δ_{H} (CDCl₃) 6.67 (s, 1 H), 3.90 (s, 3 H), 3.88 (s, 3 H) and 2.46 (s, 3 H).

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]ethanal **2i** was prepared by the literature method^{6b} in 70% yield.

Preparation of 4,5-dimethyl- and 4,5-dimethylthio-1,3-dithiol-2-ylidene derivatives **2j–2m**. General procedure.

To a stirring solution of the appropriate Wittig reagent **5**⁷ or **6**⁸ (1.0 equiv.) in dry THF (50 ml) at –78 °C under nitrogen was added butyl lithium (1.6 M solution in hexane) (1.2 equiv.) and the solution stirred at –78 °C for 0.5 h. A solution of the appropriate aldehyde (1.1 equiv.) was then added dropwise and stirring continued at –78 °C for 1 h, the solution was allowed to warm to room temperature overnight. The solution was poured into water (150 ml) and extracted with chloroform. The solvent was removed under vacuum and the resulting product was purified by column chromatography on silica gel. The following products were thereby obtained.

(4,5-Dimethyl-1,3-dithiol-2-ylidene)phenylmethane **2j** an off-white solid (50% yield), mp 60–62 °C (Found: C, 65.1; H, 5.5. C₁₂H₁₂S₂ requires C, 65.4; H, 5.5%) *m/z* (EI) 220 (M⁺); ν_{\max} (KBr)/cm⁻¹ 2913, 2850, 1596, 1576, 1551 and 1440; δ_{H} (CDCl₃) 7.2 (m, 5 H), 6.46 (s, 1 H), 1.99 (s, 3 H) and 1.98 (s, 3 H).

(4,5-Dimethyl-1,3-dithiol-2-ylidene)(2,4-dinitrophenyl)methane **2k** a dark purple solid (87% yield), mp 198–200 °C (sub.) (Found: C, 46.5; H, 3.4; N, 9.2. C₁₂H₁₀N₂O₄S₂ requires C, 46.4; H, 3.3; N, 9.0%) *m/z* (CI) 311 (M⁺ + 1); ν_{\max} (KBr)/cm⁻¹ 1597, 1576, 1500, 1453, 1320, 1300 and 1259; δ_{H} (CDCl₃) 8.76 (d, *J* 2 Hz, 1 H), 8.34 (dd, *J* 9 and 2 Hz, 1 H), 7.73 (d, *J* 9 Hz, 1 H), 7.15 (s, 1 H), 2.10 (s, 3 H) and 2.08 (s, 3 H).

(4,5-Dimethylthio-1,3-dithiol-2-ylidene)(2-pyridyl)methane **2l** a yellow oil (32% yield), *m/z* (EI) 285 (M⁺) (HRMS found 284.9771; C₁₁H₁₁NS₄ requires 284.9774); ν_{\max} (neat)/cm⁻¹ 2917, 1582, 1532, 1494, 1465, 1421, 1314, 1216 and 1147; δ_{H} (CDCl₃) 8.62 (m, 1 H), 7.51 (td, *J* 8.0 and 1.8 Hz, 1 H), 6.95 (m, 2 H), 6.56 (s, 1 H), 2.46 (s, 3 H) and 2.41 (s, 3 H).

(4,5-Dimethylthio-1,3-dithiol-2-ylidene)(phenyl)methane **2m** a yellow–brown oil (30% yield), *m/z* (EI) 284 (M⁺) (HRMS found 283.9965; C₁₂H₁₂S₄ requires 283.9822); ν_{\max} (neat)/cm⁻¹ 2916, 2848, 1595, 1578, 1496, 1441 and 1427; δ_{H} (CDCl₃) 7.28 (m, 5 H), 6.49 (s, 1 H), 2.45 (s, 3 H) and 2.43 (s, 3 H).

Preparation of nitrosated derivatives **3**. General procedure.

To a stirring solution of the appropriate (1,3-dithiol-2-ylidene)methane derivative **2** (200 mg) in dichloromethane at 0 °C was added isoamyl nitrite (3-methylbutyl nitrite) (2 ml, 15 mmol, excess) and the solution was stirred at 0 °C for 5 min. The solution was then allowed to warm to 20 °C and stirring was continued for a further 45 min. The solution was concentrated under vacuum and the addition of cold methanol precipitated the required product. Recrystallisation was achieved from methanol–dichloromethane. The following products were obtained.

Table 2 Crystal data for compounds **3g**, **3h** and **3i**

Compound	3g	3h	3i
Formula	C ₁₃ H ₁₀ N ₂ O ₅ S ₂	C ₁₀ H ₉ NO ₆ S ₂	C ₁₁ H ₁₀ N ₂ O ₅ S ₄
<i>M</i>	338.35	303.30	314.45
Symmetry	Monoclinic	Monoclinic	Triclinic
<i>a</i> /Å	22.551(9)	7.452(1)	7.690(1)
<i>b</i> /Å	9.512(4)	15.911(3)	8.637(1)
<i>c</i> /Å	13.669(6)	11.330(2)	10.536(1)
<i>a</i> °	90	90	103.64(1)
<i>β</i> °	107.53(1)	107.75(1)	92.43(1)
<i>γ</i> °	90	90	98.72(1)
<i>U</i> /Å ³	2796(2)	1279.4(4)	668.9(1)
Space group	<i>P</i> ₂ / <i>c</i>	<i>P</i> ₂ / <i>c</i>	<i>P</i> $\bar{1}$
<i>Z</i>	8	4	2
<i>F</i> (000)	1392	624	324
μ (Mo-K α)/cm ⁻¹	4.1	4.4	7.0
<i>D</i> _f /g cm ⁻³	1.61	1.58	1.56
Crystal size/mm	0.25 × 0.4 × 0.5	0.2 × 0.24 × 0.44	0.1 × 0.2 × 0.54
Scan mode	ω	2 θ / ω	2 θ / ω
2 θ _{max} /°	46.5	50	50
Data total	10 766	3019	2894
Data unique	3982	2249	2334
Data observed ^a	3560	1762	1963
<i>R</i> _{int} (<i>F</i> ²)	0.050	0.024	0.016
No. of variables	406	178	175
<i>wR</i> (<i>F</i> ²), all data	0.118	0.090	0.078
Goodness-of-fit	1.06	1.06	1.02
<i>R</i> (<i>F</i>), obs. data	0.043	0.033	0.028
Weights, ^b A, B	0.083, 0	0.053, 0.0159	0.05, 0
$\Delta\rho$ _{max} /e Å ⁻³	0.78	0.23	0.34
$\Delta\rho$ _{min} /e Å ⁻³	-0.34	-0.27	-0.21

^a $F^2 > 2\sigma(F^2)$. ^b Weighting scheme, $w^{-1} = \sigma^2(F^2) + (AP)^2 + BP$, where $P = (F_o^2 + 2F_c^2)/3$, for negative F_o^2 , $P = 2F_c^2/3$.

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene](2,4-dinitrophenyl)nitrosomethane **3c** green crystals (48% yield), mp 156–157 °C (Found: C, 39.0; H, 2.0; N, 9.6. C₁₄H₁₀N₃O₉S₂ requires C, 39.3; H, 2.1; N, 9.8%) *m/z* (CI) 428 (M⁺ + 1); ν_{\max} (KBr)/cm⁻¹ 1749, 1734, 1538, 1349 and 1264; δ_{H} (CDCl₃) 8.83 (d, *J* 3 Hz, 1 H), 8.43 (dd, *J* 11 and 3 Hz, 1 H), 7.70 (d, *J* 11 Hz, 1 H), 7.08 (s, 1 H), 3.91 (s, 3 H) and 3.88 (s, 3 H).

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene](2,6-dichlorophenyl)nitrosomethane **3d** green crystals (27% yield), mp 179–180 °C (Found: C, 41.4; H, 2.2; N, 3.3. C₁₄H₉NO₅S₂ requires C, 41.4; H, 2.2; N, 3.5%) *m/z* (EI) 407 (M⁺ + 1); ν_{\max} (KBr)/cm⁻¹ 1749, 1734, 1608, 1538 and 1193; δ_{H} (CDCl₃) 7.60 (m, 3 H), 4.02 (s, 3 H) and 3.94 (s, 3 H).

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene](2-pyridyl)nitrosomethane **3g** green crystals (50% yield), mp 214–215 °C (Found: C, 46.4; H, 2.9; N, 8.3. C₁₃H₁₀N₂O₅S₂ requires C, 46.2; H, 3.0; N, 8.3%) *m/z* (EI) 338 (M⁺); ν_{\max} (KBr)/cm⁻¹ 1840, 1740, 1536, 1514, 1503 and 1269; δ_{H} (CDCl₃) 8.80 (m, 2 H), 7.95 (m, 1 H), 7.35 (m, 1 H), 4.04 (s, 3 H) and 4.01 (s, 3 H).

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1-nitrosopropan-2-one **3h** green crystals (45% yield), mp 118.0–118.5 °C (Found: C, 39.4; H, 2.9; N, 4.4. C₁₀H₉NO₆S₂ requires C, 39.6; H, 3.0; N, 4.6%) *m/z* (EI) 303 (M⁺); ν_{\max} (KBr)/cm⁻¹ 1752, 1734, 1718, 1700, 1653, 1541, 1534 and 1261; δ_{H} (CDCl₃) 4.03 (s, 3 H), 4.02 (s, 3 H) and 3.10 (s, 3 H).

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-2-nitrosoethanal **3i** green crystals (70% yield), mp 126.5–127.5 °C (Found: C, 37.2; H, 2.3; N, 4.9. C₉H₇NO₆S₂ requires C, 37.4; H, 2.4; N, 4.9%) *m/z* (EI) 289 (M⁺); ν_{\max} (KBr)/cm⁻¹ 1774, 1735, 1651, 1400, 1268 and 1221; δ_{H} (CDCl₃) 11.05 (s, 1 H) and 4.04 (s, 6 H).

(4,5-Dimethyl-1,3-dithiol-2-ylidene)(2,4-dinitrophenyl)nitrosomethane **3k** a dark green solid (85% yield), mp 172–173 °C; *m/z* (CI) 340 (M⁺ + 1) (HRMS found 338.9980; C₁₂H₉N₃O₅S₂ requires 338.9983); ν_{\max} (KBr)/cm⁻¹ 3111, 1602.5, 1540, 1532, 1355 and 1190; δ_{H} (CDCl₃) 9.04 (d, *J* 2 Hz, 1 H), 8.64 (dd, *J* 8 and 2 Hz, 1 H), 8.06 (d, *J* 8 Hz, 1 H) and 2.41 (s, 6 H).

(4,5-Dimethylthio-1,3-dithiol-2-ylidene)-2-pyridylnitrosomethane **3l** dark brown crystals (35% yield), mp 165–166 °C; *m/z* (EI) 314 (M⁺); ν_{\max} (KBr)/cm⁻¹ 1589, 1564, 1476, 1461, 1444 and 1222; δ_{H} (CDCl₃) 8.73 (m, 2 H) 7.87 (td, *J* 7.9 and 2.0 Hz, 1 H), 7.30 (m, 1 H) 2.67 (s, 3 H) and 2.68 (s, 3 H).

(4,5-Dimethylthio-1,3-dithiol-2-ylidene)phenylnitrosomethane **3m** dark brown solid (82% yield), mp 167–169 °C (Found: C, 45.7; H, 3.5; N, 4.3. C₁₂H₁₁NOS₄ requires C, 46.0; H, 3.5; N, 4.5%) *m/z* (CI) 314 (M⁺ + 1); ν_{\max} (KBr)/cm⁻¹ 2992, 2115, 1495, 1458, 1185 and 1120; δ_{H} (CDCl₃) 7.9–7.5 (m, 5 H) 2.66 (s, 3 H) and 2.53 (s, 3 H).

X-Ray crystallography

Single-crystal X-ray diffraction experiments were carried out at room temperature, using graphite-monochromated Mo-K α radiation. All three structures were solved by direct methods, using SHELXS-86 programs¹⁷ and refined by full-matrix least squares against *F*² of all data, using SHELXL-93 software.¹⁸ All non-H atoms were refined with anisotropic displacement parameters; pyridyl H atoms were treated as ‘riding’, methyl groups refined as ‘rotating bodies’ with a common refined *U*_{iso} for three hydrogens. No absorption correction was applied. Crystal data and experimental details are listed in Table 2; atomic coordinations and thermal parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre, see Information for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/23.

For **3g**, three sets of data were collected from different samples: the principal one with a Siemens CCD area detector (see data in Table 2) and two much weaker ones on a Rigaku AFC6S four-circle diffractometer, with slightly different lattice parameters, viz. *a* = 22.593(5), *b* = 9.523(2), *c* = 13.684(3) Å, β = 107.63(3)° and *a* = 22.599(5), *b* = 9.522(2), *c* = 13.688(3) Å, β = 107.58(3)°, respectively. All three samples proved to be systematic twins with rigorously coinciding reflections (*i.e.* twin-lattice symmetry¹⁹), twinning plane (1 0 $\bar{2}$) and transformation

$a' = a + c$, $b' = b$, $c' = -c$ between the components. Twinning is clearly due to the presence of an orthorhombic C pseudolattice, which relates to the actual monoclinic P lattice of **3g** via a transformation $a' = c$, $b' = -2a - c$, $c' = -b$ and has $b' = 43.0 \text{ \AA}$ and $\gamma' = 90.1^\circ$. Surprisingly, all three samples have essentially the same (but not rational) component ratio, with the minor component contributions refined to 34.7(1), 35.0(5) and 34.6(4)%, respectively. Azimuthal scans exhibited insignificant variation, $T_{\min} : T_{\max} = 0.88$. It is noteworthy that the structure contains two crystallographically independent, but essentially identical, molecules, which are related by a pseudoglide plane parallel to the twinning plane (1 0 -2), intersecting the z axis at $z = 1/8$ (for the reference molecules) and having the shift of $0.5a - 0.35b$. This 'transformation' and the structure at large are incompatible with the orthorhombic symmetry even approximately. However, as the molecules are arranged in layers, parallel to the twinning plane, with the interlayer separation of *ca.* $c/4$, the Laue symmetry of the samples is close to orthorhombic. Thus, for the CCD data, $R_{\text{int}}(F^2) = 0.138$ for 8516 'orthorhombic' equivalents, vs. 0.050 for 6784 'monoclinic' equivalents. The final difference Fourier map for this experiment shows three outstanding residual peaks of electron density ($0.7 < \Delta\rho/e \text{ \AA}^{-3} < 0.8$, the rest being under $0.35 e \text{ \AA}^{-3}$), close to O(3B), C(8A) and S(2A), which could not be rationalised.

The structure of **3g**, obtained from the CCD experiment, was refined in the same way against both sets of diffractometer data. The first one gave $R(F) = 0.052$ for 1950 observed data [$F^2 > 2\sigma(F^2)$] and $wR(F^2) = 0.170$ for 2587 total data with $2\theta < 50^\circ$, max. $\Delta\rho = 0.43 e \text{ \AA}^{-3}$; the second one converged at $R(F) = 0.041$ for 1629 observed data and $wR(F^2) = 0.121$ for 2171 total data with $2\theta < 50^\circ$, max. $\Delta\rho = 0.36 e \text{ \AA}^{-3}$.

For **3h** and **3l**, the experiments were carried out on a Siemens P4 four-circle diffractometer. For **3l**, empirical extinction correction factor $[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ was applied, with x refined to 0.069(5); in this structure the C(5)H₃ methyl group is disordered over two positions (A and B), 0.32 Å apart, which were independently refined with occupancies of 60 and 40%, respectively. Short intermolecular distances C(5A)⋯C(5A) 3.31 and C(5A)⋯C(5B) 3.48 Å between inversionally related molecules suggest concerted motion (distribution) of their disordered groups.

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